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PROPELLANTS SEMINAR

13-14 June 1956

LIQUID PROPELLANTS

(With Appendixes Containing the Previously Unpublished Proceedings
on Solid Propellants)

(Edited Transcript)

30 April 1957

ECONOMIC DEFENSE INTELLIGENCE COMMITTEE

WORKING GROUP ON PROPELLANTS AND FUEL ADDITIVES

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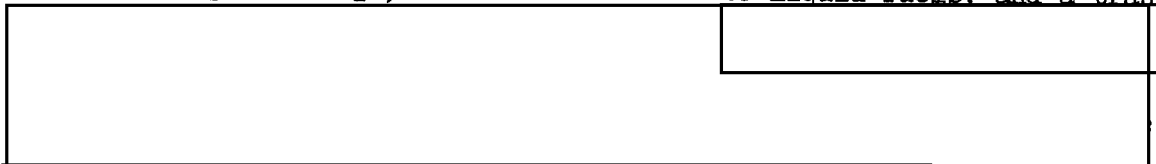
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FOREWORD

On 13 and 14 June 1956 a "Propellants Seminar" was held under the sponsorship of the Working Group on Propellants and Fuel Additives of the Economic Defense Intelligence Committee (EDIC). The purpose of the seminar was to establish in this highly strategic and rapidly developing fuels field a common basis of technical knowledge for, and to promote the mutual appreciation of the informational requirements of, technicians, intelligence officers, and action-agency representatives concerned with intelligence support activities for the US economic defense program.

The following report consists of a tape-recorded transcript of the first day's proceedings, which were devoted to liquid fuels, and a tran-



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The presentation on solid propellant technology as transcribed in this report was made by a member of the staff of the Air Technical Intelligence Center. The classification of the seminar was [redacted] to afford an opportunity to handle all available information, although many individual items were of a lower classification. All of the speakers at the seminar have reviewed the literal transcript of their remarks and have approved the present report.

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The reaction to the seminar of participants from the intelligence community and action agencies seems to speak strongly for other EDIC working groups with similar exploratory assignments to schedule similar initial information sessions when novel and complicated technical developments are involved.

As regards the timeliness of the Propellants Seminar, it should be noted that the presentations covered, among other things, information developed in support of the US delegation as background for negotiations which resulted, in the fall of 1956, in the embargo to the Soviet Bloc of boron materials by COCOM participating countries, the only major embargo action in COCOM since 1954.

1 March 1957

- iii -

S-E-C-R-E-T

Next 2 Page(s) In Document Exempt

S-E-C-R-E-T

LIQUID PROPELLANTS

I. Introduction.

A. Definitions.

I will define some of the elements that we are going to talk about. I will quote from Sutton* first, and then I will try to simplify this. According to Sutton a rocket is a means of jet propulsion, and jet propulsion is a means of locomotion whereby a reaction is imparted to a device by the momentum of ejected matter.

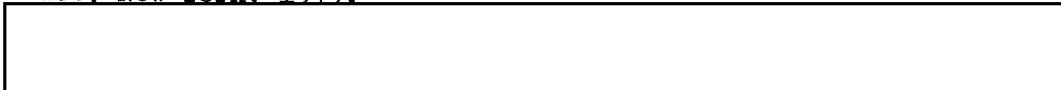
There are two types of jet propulsion with which we are primarily concerned. One is the rocket, and the other is the ducted jet. The major difference in principle is that the rocket carries all of its energy self-contained in the sense that its oxidizer is a part of the unit, whereas in the ducted jets air is utilized for oxidation. Now, a propellant can be a fuel or an oxidizer. They are the materials that provide the energy which propels the device.

The full interest in rockets, of course, develops out of their ability to move at high speed which, in turn, requires that the rate of expenditure of energy be high. I make these remarks simply by way of orientation for background for those of you who may not have thought about it.

I have some slides here which show some of the basic types of jet-propelled devices.** Figure 1 is a diagram of a pulsejet. It is similar to a rocket, as you will see later, except that the oxidizer, in this case air, passes into the chamber from the front end (the direction of motion being to the left) through the valve which intermittently closes. When it is closed, fuel is injected and burned in a chamber that is closed at the front end, as with a rocket. The valve would then open, the air would sweep out the chamber, and the cycle would be repeated.

Figure 2 is a diagram of a ramjet. Again this is similar, except that there is no valve in the front end; it is always open.

* Sutton, G.P., Rocket Propulsion Elements, John Wiley and Sons, Inc., New York. 1949.



S-E-C-R-E-T

S-E-C-R-E-T

This device depends on having achieved a certain velocity in flight, so that the forward motion (to the left again) tends to compress the air which then passes back, mixed with the fuel. Combustion occurs, and the missile is propelled.

Figure 3 shows a turbojet, which is similar to the ramjet except that a turbine driven by the combustion products is connected by a shaft to a compressor, so that, as combustion occurs, the shaft rotates the compressor. This compresses the air, which is pulled in through the front end. The major advantage of this device is that, with the compressor, there is no need to achieve a particular velocity before efficient performance is obtained from this device. This shaft can be extended further and a propeller placed on it, making a turboprop engine.

Finally, in Figure 4 we have the rocket, and, as you can see, there is no opening in the front end. The materials that react are contained within the rocket, and the combustion products pass out the rear. The reaction of the combustion and the passage of the gases out through the back drive the rocket forward.

Figure 5 provides a general idea of the size and shape of a combustion chamber. In this case, the fuel enters at the upper left and the oxidizer at the lower left. They are mixed at the left side of the combustion chamber; combustion occurs. There is a nozzle constriction at the outlet to increase the pressure within the combustion chamber. The gases then expand through the nozzle and pass out to the right (the direction of motion being to the left).

Figure 6 shows a V-2 motor, a German development during World War II, which was one of the first operational rockets of this type.

Figure 7 is a schematic diagram of a pressurized bipropellant rocket system. Gas contained under pressure in the center vessel is fed into a fuel tank on the left and an oxidizer tank on the right. The pressure of the gas drives the two fluids through the control valves into the rocket motor.

Figure 8 shows essentially the same thing except that instead of using a pressurized gas the propellants are moved by a pump which,

S-E-C-R-E-T

in turn, is driven by a turbine. The turbine is powered by using a portion of the rocket propellants or a special propellant for that purpose.

An important design variable in a rocket motor is the injection system whereby the fuel and oxidizer are introduced into the combustion chamber and mixed. Nine different types of injection and mixing devices are shown schematically in Figure 9.

Because of the short life of most structural materials in contact with the propellants and combustion products at combustion chamber temperatures, it is desirable to keep the walls of the combustion chamber as cool as possible. A schematic diagram of such a cooled-wall chamber is shown in Figure 10. The coolant may be one of the propellants, in which case the energy removed by the coolant is later recovered as the propellant is burned. This is called "regenerative cooling."

B. Criteria for Selecting a Rocket Propellant.

In the previous section a description of the manner in which rocket motors operate was given. In general, the method of operation can be stated concisely as follows. Liquid propellants, either a monopropellant or an oxidizer-fuel combination, are fed under pressure through an injector into the combustion chamber. In the combustion chamber the propellants combine chemically in the case of a fuel-oxidizer combination or decompose in the case of the monopropellants. The net effect is to produce hot combustion gas under pressure. These pressurized combustion gases then expand through the nozzle. Thrust is produced by the force developed in accelerating these gases to a high velocity.

The performance of a rocket vehicle, of course, depends on things other than the performance of the rocket motor or rocket propellant system itself. The performance also depends on the ability of the vehicle designers to design an efficient, light-weight structure and upon the amount of payload that the rocket vehicle must carry.

S-E-C-R-E-T

In comparing the performance of various rocket propellant systems, it has proved convenient to have some numerical criterion of performance. This criterion is called "specific impulse." Specific impulse, in simple terms, is the number of pounds of force developed per pound of propellant burned per second. The rocket designer is interested in having a high value of specific impulse, since this means more efficient utilization of the propellants which the rocket carries. The mathematical expression for specific impulse is as follows:

$$I_s = K \sqrt{\frac{T_c}{M}} F$$

where I_s = specific impulse, lb force-sec/lb mass (often stated sec)

K = a numerical constant of appropriate units

T_c = absolute temperature of combustion products in chamber before expansion, R

M = average molecular weight of exhaust products, lb/mole

F = a variable which is a function of the exhaust products, temperature level, and expansion ratio

It is obvious from inspection of this equation that the important variables will be the absolute chamber temperature, T_c , and the average molecular weight, M , of the exhaust products. F is a function of the composition of the exhaust gases, their temperature level, and the expansion ratio for the rocket nozzle. It is a relatively weak function and is approximately the same for all propellant systems operating at the same chamber pressure. The chamber temperature, T_c , appears in the numerator, and so a high value is desirable. T_c depends primarily on the heat of combustion of the rocket propellants, so that propellants having high values for the heat of combustion are required. Since the average molecular weight, M , appears in the denominator, a low value for this quantity is needed. Compounds made up of elements having low atomic weights are desirable as rocket propellants, since this means that the exhaust products generated will have low average molecular weights.

S-E-C-R-E-T

Thus desirable liquid rocket propellants, either fuel plus oxidizer or monopropellants, will have the properties of high heats of combustion (or decomposition in the case of monopropellants) and be composed of elements having low atomic weights.

Unfortunately, propellants having high specific impulses must also have other desirable properties if they are to be used in rocket-propelled vehicles. This can best be explained by considering the factors which affect the range of a rocket-propelled vehicle. An approximate equation for the range of a rocket vehicle is as follows:

$$R_{\max} = I_s^2 g^2 + \ln \frac{W_b^2}{W_o}$$

where $R_{\max}$ = maximum range, ft

I_s = specific impulse lb force-sec/lb mass

g = acceleration of gravity, ft/sec²

W_o = mass of rocket at launching, lb M

W_b = mass of rocket after fuel is expended, lb M

This equation is only approximate and can be greatly in error for long ranges on curved surfaces which, of course, are of concern to us since the surface of the earth is curved. However, an inspection of the variables in the equation will provide a great deal of insight into the problems of rocket design.

For all other things equal, the range of any vehicle will be proportional to the square of the specific impulse. For example, a missile using a propellant system having a specific impulse of 300 will have over twice the range of one using a system with a specific impulse of 200. This further illustrates the importance of specific impulse as a criterion for a propellant system.

S-E-C-R-E-T

The mass of propellant which is carried in a rocket is the difference between the mass of the rocket at launching and the mass of the rocket after fuel is expended -- that is, $W_0 - W_b$. An increase in the amount of fuel contained in a rocket vehicle decreases the ratio W_b over W_0 and increases the maximum range. Consequently, the rocket designer is always trying to increase the mass of the rocket propellant which can be carried. However, he has certain limitations, since W_b must include the mass of the payload, the structures, the tanks, as well as the rocket engine and any auxiliary equipment. Any guidance or control equipment is also included as a part of W_b . To minimize W_b , much ingenuity must be exercised by the rocket designer. To assist him in this, propellants should be compact. Consequently, we find that high density is an important consideration. Also, propellants which have low vapor pressures, thereby requiring thinner tank walls, and those which are liquid at ambient temperatures, thus requiring no insulation, are the most desirable. Unfortunately, most propellants which produce low molecular weight exhaust products have a low density or are not liquids at ambient temperatures.

Figure 11 summarizes the desirable properties for propellants. Most of these desirable properties are ones which are obvious from the present discussion or from commonsense considerations. Others such as item 12 are necessary for engineering design purposes or for compatibility with missile guidance component operation (item 13). Safety (items 6 and 10) is another important criterion. Further consideration of these points will be given in later sections where specific propellants are discussed.

In summary, then, the desirable properties of liquid rocket propellants are: high heat of combustion (or decomposition), low molecular weight exhaust products, high liquid density, low vapor pressure, and a high boiling point. The criteria of high heat of combustion and low molecular weight exhaust products are usually not considered individually but are considered in combination as expressed in the specific impulse relation.

S-E-C-R-E-T

II. Monopropellants.

A monopropellant is a material which may, under appropriate conditions, undergo a self-sustaining exothermic (energy-releasing) reaction. Because of the inherent thermodynamic instability of monopropellants, the tendency toward decomposition is always present. The problems concerning the most efficient use of monopropellants, therefore, involve close control of the energy-producing decomposition reactions. Such close control must be manifested not only during the actual application to obtain the highest useful energy yield and conversion, but also in the handling, storage, and other treatments prior to actual use. It may be seen, then, that the use of a monopropellant for any particular purpose involves a close balancing of many diverse factors. Some of these factors are shown in Figure 12.

Of course it must be realized that for any desired application, certain monopropellant characteristics will be relatively more important than others. For example, for gas generators (a major monopropellant application) the monopropellant should give low reaction temperatures (1800°F) and an exhaust stream free of solid particles. It is necessary that these criteria be met even at the expense of specific impulse. Hence the wide application of monopropellant hydrogen peroxide (chamber temperature, 1360°F , and specific impulse, 132 lb-sec/lb) to gas generators. On the other hand, for ram-rocket applications the monopropellant should give a high specific impulse in order to provide the necessary thrust during acceleration. In addition, the rocket exhaust must possess sufficient chemical energy (high heat of combustion) to act as a fuel source during the ramjet stage of flight operation, with a minimum volume of air for combustion. Thus the interest in methyl-acetylene (specific impulse, 190 lb-sec/lb and C + H exhaust products) for ram rockets. From these examples, it is obvious that no single monopropellant can meet the requirements for all conceivable monopropellant applications. Figures 12 and 13 show the monopropellants that have received most consideration in terms of actual use, past research and development effort, and future interest.

A. Hydrogen Peroxide.

Hydrogen peroxide has one of the longest histories of the liquid propellants. Before World War II, considerable development work had been done on hydrogen peroxide in Germany. By 1938 the Germans were producing concentrated hydrogen peroxide, which they used in a variety of weapons during the war, including the first operational piloted rocket

S-E-C-R-E-T

airplane ever flown, the Messerschmitt, Me 163. Following the war, production of concentrated hydrogen peroxide in Germany was banned as one of the provisions of the Allied Control Commission to regulate the military potential of defeated Germany. A great deal of work, however, has been carried on and expanded in both England and the United States.

Monopropellant hydrogen peroxide has been used for gas generators in large rockets, for submarine and torpedo propulsion, for rocket assist takeoff units, and as a source of auxiliary power for helicopters.

Some of the major reasons for its use as a monopropellant are as follows: (1) simplicity of the monopropellant system, (2) ease with which it can be catalytically decomposed into oxygen and steam, and (3) reliability of operation.

1. Physical Properties.

Formulas H_2O_2 and $H_2O_2 + H_2O$. Molecular weight 34.

Hydrogen peroxide solutions ranging from 50 to 100 percent by weight are of interest in propulsion applications. Ninety percent peroxide and 76 percent peroxide have received major consideration: 90 percent as an oxidizer and rocket propellant and 76 percent for gas generator applications. Ninety percent hydrogen peroxide has the advantage of a higher specific impulse and a higher density, but the disadvantage of a higher freezing point. Seventy-six percent peroxide has a lower freezing point and a lower flame temperature, which are quite important for gas turbine applications. Some of the more important properties of these solutions are given below:

	90 Percent H_2O_2	76 Percent H_2O_2
Freezing point	12°F	-23°F
Boiling point	284°F	266°F
Density, liquid	1.4 g/cu cm at 68°F	1.3 g/cu cm at 68°F
Vapor pressure	Negligible	Negligible
Energy of decomposition	ca. 23 kilo-cal/g mole	ca. 23 kilo-cal/g mole

S-E-C-R-E-T

2. Performance.a. Monopropellant.

<u>H₂O₂</u>	<u>Chamber Pressure, P_c, psia</u>	<u>Specific Impulse, I_s, lb-sec/lb</u>	<u>Density Impulse, I_s</u>	<u>Chamber Temperature, T_c, °F</u>
90 percent	300	132	190	1,360
75 percent	300	105	138	690

As a monopropellant, hydrogen peroxide requires a decomposition catalyst. In the past, calcium permanganate solutions have been used as well as catalyst stones (high-temperature treated cement stones incorporating manganese, chromium, and lead). The present emphasis in this country is on the development of silver screen catalysts.

b. Bipropellant.(1) Comparison with Different Fuels.

<u>99.6 H₂O₂</u>	<u>Chamber Pressure, P_c, psia</u>	<u>Specific Impulse, I_s, lb-sec/lb</u>	<u>Density Impulse, I_s</u>	<u>Chamber Temperature, T_c, °F</u>
93 percent				
EtOH	500	240	320	4,600
JP-4	500	248	320	4,830
Hydrazine	500	265	325	4,690

(2) Comparison with Different Oxidizers.

<u>JP-4</u>	<u>Chamber Pressure, P_c, psia</u>	<u>Specific Impulse, I_s, lb-sec/lb</u>	<u>Density Impulse, I_s</u>	<u>Chamber Temperature, T_c, °F</u>
H ₂ O ₂	500	248	320	4,830
RFNA	500	240	310	5,150
LOX	500	265	260	5,770

Hydrogen peroxide is a moderate performance oxidizer but is not self-igniting with most fuels.

S-E-C-R-E-T

3. Materials and Handling.

Concentrated hydrogen peroxide reacts vigorously on contact with many inorganic compounds such as potassium permanganate and ferrous sulfate and with many organic compounds such as hydrazine, carbonyls, and phenolics. Its decomposition is catalyzed by many substances, among which are oxides of manganese, cobalt, lead, and silver; and by metals, such as platinum, silver, lead, mercury, manganese, cobalt, and others. However, in suitable containers free of contaminants, hydrogen peroxide can be kept for long periods of time.

a. Materials Good for Long-Time Contact.

99.6 percent Al and 2S Aluminum Alloy

Polyethylene, Teflon, Kel-F

Fluorolubes, Kel-Flo Polymers, Perfluorolube Oils,
Hydrocarbon Oils

b. Materials Good for Short-Time Contact.

Aluminum 43, 52S, 56S, 61S, 63S, 150S

Stainless Steels 303, 304, 309, 310, 316, 317, 318,
321, 322, 347

Durimet 20

Koroseal, Polystyrene, Vinylite, Reloform

Pumps should be of self-priming centrifugal type made of cast aluminum-alloy 43. Teflon packing and fluorolube lubricant should be used. Tanks may be made of 99.6 percent aluminum, heliarc-welded with pure aluminum. Tanks in missiles can be of collapsible plastic, such as vinylite Vu 1930, if the peroxide is to be stored for only a few days. Polyethylene shows no change even after long exposure. Spring-loaded check valves with Teflon pintle and packless bellows valves with Teflon disk which seats on SS 347 are in current usage. Valves larger than 1 inch should be flanged.

S-E-C-R-E-T

4. Passivation of Materials to Be Used with Hydrogen Peroxide.

Plastics can be prepared by scrubbing with a synthetic soap solution. Aluminum should be degreased by scrubbing with detergent, then treated with dilute sodium hydroxide (NaOH), then with sulfuric acid (H₂SO₄), and finally rinsed with distilled water. Stainless steel should be degreased and passivated with a nitric acid solution. All equipment should be flushed (rinsed) with dilute hydrogen peroxide before placing in concentrated peroxide service.

5. Stability.

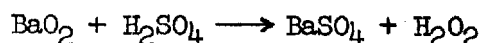
If above precautions are followed, concentrated peroxide solutions are quite stable at ambient temperatures. At temperatures greater than 100°F, however, decomposition becomes more rapid. Hydrogen peroxide is not sensitive to shock.

The addition of stabilizers is recommended for controlling trace impurities present in hydrogen peroxide solutions. Tin is added as sodium stannate or hydrous stannous oxide to absorb heavy metallic ions. Phosphates are used to complex heavy metal ions. These stabilizers are added in the order of parts per million.

6. Production Methods.

a. Barium Peroxide Method.

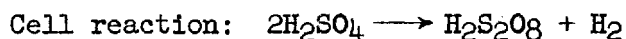
Six to 8 percent hydrogen peroxide prepared by the reaction between barium peroxide and 70 percent sulfuric acid plus a few percent of phosphoric or hydrochloric acid.



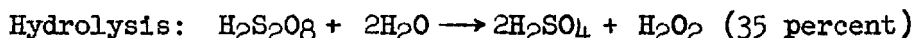
This process is reported to be used by only one US company (Westvaco) and accounts for 10 percent of annual production.

S-E-C-R-E-T

b. Electrolytic Process.



(Peroxysulfuric acid)



Ninety percent hydrogen peroxide is obtained by distillation and rectification. This process requires high capital investment and high electrical requirements. In addition, chemicals and electrolytes must be of high purity.

c. Nonelectrolytic Process.

The reported basis for Du Pont's new hydrogen peroxide processes is to take an oxidizable "carrier," or organic hydroxyl compound such as anthraquinone, oxidize it to a pure state, then decompose it to a ketone, with hydrogen peroxide being evolved. The ketone is then hydrogenated back to the hydroxyl state and is ready for recycling. Very little information is available in respect to process variables such as the nature of the organic starting materials, solvent, catalyst, and method of oxidation. The advantages of this process are a lower capital cost of plant and simpler plant operation. Shell is reported to be using the liquid-phase oxidation of isopropyl alcohol with oxygen at pressures greater than atmospheric and at a temperature range of 194° to 284°F. Nonelectrolytic processes should bring the cost of peroxide down. Technical know-how, however, is very important in these processes.

7. Sources of Information.

The following organizations have had extensive experience with hydrogen peroxide: the Buffalo Electrochemical Co., the Bureau of Aeronautics, the MIT-Hydrogen Peroxide Laboratories, and the E.I. du Pont de Nemours & Co. Both Shell Chemical and Columbia-Southern are entering the field with nonelectrolytic processes.

8. Miscellaneous Application of Hydrogen Peroxide.

An interesting application of hydrogen peroxide as a monopropellant to provide auxiliary power for helicopters has been recently developed. This work was done by Reaction Motors under sponsorship of

S-E-C-R-E-T

S-E-C-R-E-T

the Bureau of Aeronautics of the Department of the Navy. Hydrogen peroxide is carried in a tank on the rotor shaft and fed by centrifugal force to a small catalyst chamber mounted on the tip of each rotor. There it is decomposed, and the exhaust jet is used to provide additional driving power for the rotor. This system was applied to a Sikorsky helicopter used by the Marine Corps. The entire weight of the filled hydrogen peroxide system is about 350 pounds, including about 280 pounds of 90 percent hydrogen peroxide. With this auxiliary power, the payload, the rate of ascent, and the hovering ceiling of the helicopter are greatly increased, and the permissible area for landing, in case of failure of the main powerplant, is increased at least fourfold.

B. Ethylene Oxide.

Ethylene oxide has a boiling point of 51°F, which is undesirably low, and a freezing point of minus 171°F. To keep it as a liquid within the range of normal temperatures, some pressure is required. Its density is 0.9 g/cu cm. Ethylene oxide is easy to handle, and military regulations suggest that ethylene oxide be handled like aviation gasoline. Fumes from the liquid are to be avoided. Ethylene oxide forms a wide range of explosive mixtures with air from 3 to 100 percent ethylene oxide. Ethylene oxide has a specific impulse of 159 to 168 sec. Catalytic ignition does not appear possible.

The materials for the production and storage of ethylene oxide are usually steel, stainless steel, or glass. Corrosion is not a problem, but some materials (acids, bases, chlorides, and oxides) increase the rate at which ethylene oxide polymerizes.

Two commercial methods of production are employed. The earlier process involves the reaction between ethylene, which is found in natural gas, and hypochlorous acid, which is formed from the reaction of chlorine and water. The resulting material is treated with sodium hydroxide to produce the ethylene oxide. The second process is a direct catalytic conversion of ethylene and oxygen to the oxide. Most new installations employ the second process. Production of ethylene oxide in 1953 was about 500 million pounds at a price of about 14 cents per pound. Producers include Union Carbide and Carbon, Dow Chemical, Jefferson Chemical, Wyandotte Chemical, and Mathieson Chemical.

S-E-C-R-E-T

C. Propyl Nitrate.

Both propyl nitrate and its mixture with ethyl nitrate (60 percent ethyl - 40 percent propyl) have similar properties; so they will be discussed together. Their freezing points are below minus 148°F, and their boiling points are above 211°F, thus providing a wide useful liquid range. Their density is about 1 g/cu cm. Nitrates in general are impact sensitive, and these nitrates are no exceptions. Some explosions have occurred with these materials. Unfortunately, propyl nitrate and its mixture corrode ordinary steel, but stainless steel and aluminum can be used with them.

Production methods involve just a simple nitration of the corresponding alcohol. Propyl alcohol, isopropyl alcohol, and ethyl alcohol are available commercially in large quantities, and the nitration step is a well-known operation. The production is almost insignificant. The British have done a great deal of work with the isopropyl nitrate, whereas in this country the normal propyl nitrate has received the greatest attention. The principal producer is Du Pont, although the Ethyl Corporation also is interested in these compounds.

Their specific impulse is slightly higher than that of ethylene oxide, being about 165 to 170. In summary, the two things to remember about this system are that production is very low and that the materials are sensitive to impact.

D. Hydrazine.

Another monopropellant is hydrazine. It has been given fairly wide publicity because of the important and difficult chemistry and engineering work performed in developing its manufacturing process. Some of its properties are given in Figure 12. Its molecular formula is N_2H_4 . Its freezing point is important in its use as a propellant. It is higher than that of water, and this is the main drawback in its use. The boiling point is sufficiently high, and the vapor pressure is reasonably low at ambient temperatures. Its density and viscosity are about equal to those of water. The heat of formation is in the desirable range. The monopropellant performance characteristics of hydrazine are given in Figure 13. As a monopropellant, its specific

S-E-C-R-E-T

impulse is of the order of 169. Because its density is approximately that of water, its density impulse is about the same value.

One of the drawbacks in using hydrazine as a monopropellant is that it is difficult to initiate combustion. Once it is started, it seems to proceed satisfactorily. Hydrazine is toxic, flammable, and rather expensive by our criteria at the present time.

In handling hydrazine it must be kept away from any oxidizing materials such as rust, peroxides, and copper salts. It can be stored and shipped in glass, in stainless steel, or in polyisobutylene-lined drums. These drums must be sealed tightly, and normally the drums are blanketed with nitrogen after being loaded. Other materials which are usable with hydrazine are chrome-nickel, polyvinyl chloride, natural rubber, and low-sulfur buna rubber.

The toxicity of hydrazine is relatively high. It can be absorbed through the skin, by ingestion or by inhalation, so that protective clothing and ammonia gas masks are recommended. Hydrazine is not sensitive to shock, and it is thermally stable below about 320°F.

The normal production method for hydrazine is the Raschig process, in which ammonia is reacted with sodium hypochlorite. This gives a low-concentration product which then can be concentrated. The urea process, using urea instead of ammonia, is also desirable. The cost recently is of the order of \$3.00 per pound. Some long-range estimates indicate that it might drop to as low as 50 cents a pound. It is produced by the Olin Mathieson Chemical Corporation.

Because of the high freezing point of hydrazine, a great deal of work has been done in an attempt to find additives which might lower the freezing point. Ammonium thiocyanate is one of these additives and is actually used in the present IAR air-to-air rocket. The addition of 32 percent ammonium thiocyanate to hydrazine will lower the freezing point to minus 65°F.

In addition to its use as a monopropellant, which is not very extensive, hydrazine is also used in bipropellant systems. It is used as a fuel in combination with various oxidizers. With red fuming nitric acid, its specific impulse ranges from 285 for pure hydrazine to 265 with the addition of 32 percent ammonium thiocyanate. With liquid oxygen,

S-E-C-R-E-T

hydrazine's specific impulse is about 280 and with liquid fluorine about 320.

It is obvious from a consideration of those few performance values that the bipropellant systems, in general, are significantly higher in their performance than the monopropellant systems. The monopropellant systems are used only for very specialized applications, where benefit can be derived from using only a single substance.

E. Nitromethane.

Another monopropellant, not of such importance as hydrazine, is nitromethane. Its characteristics are illustrated in Figures 12 and 13. Its freezing point is minus 20°F, a lower and more desirable value than that of hydrazine. Its boiling point is sufficiently high at 214°F, and it has a high density, about 14 percent higher than that of water. The specific impulse for this rather high-energy monopropellant is 217. Again, there are difficulties with ignition -- that is, initiating combustion. Consequently, many times a bipropellant system with liquid oxygen as an oxidizer is used to initiate combustion. Once ignited, the nitromethane is used alone as a monopropellant.

Nitromethane has good availability. It is not corrosive and has low toxicity. The major disadvantage in using nitromethane as a monopropellant is that good combustion is difficult to achieve and that large motors are required to get something approximating complete combustion.

With regard to handling, nitromethane is not classified as a dangerous material by the ICC, but it is sensitive to adiabatic compression and explodes in gunfire tests. It is usually shipped in 55-gallon drums lined with plastic. Stainless steel and plastic-coated steel are satisfactory for use, as well as other plastic materials such as Bakelite. It is incompatible with copper, tin, lead, zinc, lined steel, and many plastics.

Production of nitromethane is by vapor-phase nitration of propane, with subsequent purification by fractional distillation. Production in 1950 was 250,000 pounds per year at a cost of about

S-E-C-R-E-T

25 cents per pound. Producers are Commercial Solvents and Aerojet-General.

As with hydrazine, some research has been performed in an effort to find additives to improve the combustion characteristics of nitromethane and to desensitize it somewhat. A mixture with 20 percent ethylene oxide has shown the most promise.

F. Methyl Acetylene.

I would like to mention briefly two monopropellants that are in the research stages. As mentioned before, there has been interest in the acetylenic compounds. One of the more interesting ones is methylacetylene, or propyne, which is being developed specifically for ram-rocket applications.

This compound has a relatively low boiling point (minus 100°F), which means that it must be handled under moderate pressures as a liquefied gas. It also possesses a fairly low density (0.68 g/cu cm). Its performance is reasonably high, approaching 200 seconds, but the density impulse is quite low (118). Its high heat of combustion of the product gases makes it desirable for ram-rocket applications. It should be emphasized that it is in the early stages of research and development. It is currently selling for \$6.25 per pound; however, the predicted selling price for large-scale production runs between \$0.50 and \$1.00 per pound. Methylacetylene has certain storage and supply problems, since it is a liquefied gas, and it also has combustion problems because there are some solid combustion products occurring in the exhaust. Much of the work on the development of this compound for ram-rocket applications has been done at New York University (by Dr. Paul Winternitz). Considerable work also has been done at Princeton University.

G. Amine Nitrate Mixtures.

The other exotic compounds are the amine nitrate mixtures. The possibility of combining a fuel and an oxidizer in the same mixture in order to gain a specific impulse comparable to that of a bipropellant system has been considered at different times. Recently Dr. John Clark of the US Naval Air Rocket Test Station at Dover, New Jersey, has been working with these compounds. Phillips Petroleum also has been engaged

S-E-C-R-E-T

in development work on them. The amine nitrates have monopropellant characteristics, with specific impulse comparable to a bipropellant system, but they are quite sensitive to thermal shock. The only motor tests that have been run to date have ended with the combustion chamber exploding. So there are some problems to be solved. If this sensitivity can be controlled, however, there exist potential applications in air-to-air and ground-to-air missiles, and perhaps in Jato units. It should be emphasized again that these two compounds are in the initial research stages.

H. Summary of Monopropellants.

Figure 13 summarizes the monopropellants of current interest. The "workhorse" monopropellants are hydrogen peroxide, ethylene oxide, and propyl nitrate. Hydrogen peroxide has been used extensively in gas generators, an important application in large missiles. With a larger missile a turbopump system is used rather than the pressurized system because of the weight saving involved, since heavy high-pressure tubes are eliminated. Hydrogen peroxide is also of considerable interest as a bipropellant oxidizer, especially with JP-4 or the kerosene type of fuels. The Navy has been interested in this system because of the good burning characteristics with JP-4 and the relative ease of shipboard handling as contrasted with nitric acid.

Ethylene oxide is another monopropellant that has received much consideration. It has been used for auxiliary power sources such as aircraft starters. Likewise, normal propyl nitrate has been used for similar applications and is also finding applications in torpedo propulsion. The mixture of 60 percent ethyl nitrate and 40 percent normal propyl nitrate is also of interest as a monopropellant. Nitromethane has received attention in the past, and there is some current interest in mixtures of nitromethane and ethylene oxide. Hydrazine is of interest as a monopropellant, chiefly in the form of hydrazine - hydrazine nitrate - water mixtures which are of interest in liquid-propellant gun applications. There has been considerable work done on monopropellant systems over the past few years. Methyl acetylene and the amine nitrate mixture are still in early stages of development as far as monopropellant applications are concerned.

S-E-C-R-E-T

III. Bipropellants.

A bipropellant combination consists of an oxidizer and a fuel. We shall discuss all the oxidizers as a group and then all the fuels as a group.

A. Oxidizers.

Figure 14 is a summary of the properties of the oxidizers that we shall discuss today. These are the ones that are receiving the most attention and are probably the ones that you may encounter.

The first thing that I would like to point out on Figure 14 is that all these compounds -- oxygen, red fuming nitric acid, hydrogen tetroxide, ozone, fluorine, chlorine trifluoride, perchloryl fluoride, and tetranitromethane -- have one common property. They contain either oxygen or fluorine, both of which are good oxidizing atoms of low molecular weight. You will note that the freezing points in this list of oxidizers range from minus 362°F to plus 12°, 31°, and 57°F, and the boiling points range from minus 297° to plus 302°F.

Figure 14 shows that there is a big gap in the thermoconductivity data. The viscosities of the oxidizers are all fairly low. The densities of the oxidizers are the most important data on this chart, and they are high relative to fuels. You will note that they are all greater than 1 g/cu cm, with oxygen and fluorine the lower ones at 1.1 g/cu cm. These are the things that you should remember about these particular compounds.

1. Liquid Oxygen.

Liquid oxygen is the first oxidizer to be discussed, and, as you may have noted from Figure 14, its most undesirable property is its boiling point, which is about minus 300°F. In other words, you are most likely to encounter it as a compressed gas. In fact, if you encounter it at any temperature above minus 180°F, it will be a gas. Below these temperatures it can be liquefied, but this sets a limitation on the storage facilities. Liquid oxygen is usually contained within insulated storage facilities vented to the atmosphere. To reduce evaporation losses, the heat transfer is minimized as much as possible by insulation of the walls of the tank. In order to maintain the present supply of liquid oxygen,

S-E-C-R-E-T

it is necessary to have auxiliary equipment along with your storage facilities to contain the vapor and reliquefy it. The big problem with oxygen, therefore, is to contain it.

Oxygen does have a fairly high density and is not toxic or corrosive. However, in handling it, severe cases of frostbite can result. Because of its being so cold and because some materials are brittle at low temperatures, materials for handling liquid oxygen are limited to nickel, Monel, Inconel, copper, aluminum, 18-8 stainless steel, or annealed brass. Fortunately, storage methods have been devised so that liquid oxygen can be transported in tank cars, but this is a difficult and specialized operation. During the war, liquid oxygen was shipped to the South Pacific with reported evaporation losses of about 1/2 of 1 percent per day.

As far as production is concerned, much specialized refrigeration equipment is required to make the operation economical. This refrigeration equipment in turn requires considerable electrical power. The raw material is air, and once the air is liquefied, it is fractionated, oxygen being one of the products. The commercial production in 1943 was about 112,000 tons. It is produced at a cost of about 2 to 4 cents per pound, which makes it one of the least expensive materials that we have been considering.

Because of its low cost and because it is so readily available, liquid oxygen, in spite of its disadvantages in handling, remains a very important oxidizer. Historically, the Germans used oxygen in their V-2 missiles, and, because of the technology that they had built up, much of the rocket work in this country after World War II was concerned with it. The major producers of this material include Linde Air, Air Reduction, Liquid Carbonic, Olin Mathieson, and Air Products. There are other companies that make equipment to produce liquid oxygen. Some industrial consumers buy liquid oxygen, but most large consumers buy a "packaged" liquid-oxygen plant which the supplying company maintains.

The industrial uses of liquid oxygen should also be mentioned. It is used in large quantities for the production of steel, some of which is high-pressure gaseous oxygen, but similar facilities are needed for its production. A sustained major missile-launching program may put a strain on steel production or limit its increase. Another use of oxygen that is somewhat more restricted but is interesting is

S-E-C-R-E-T

its use as an explosive. If liquid oxygen is mixed with carbon or carbonaceous materials, the combination becomes an explosive which is used in such operations as mining and quarrying. This is mentioned to indicate that contact with carbonaceous materials should be avoided when handling liquid oxygen.

When speaking of performance, it is necessary to specify the fuel as well as the oxidizer. The specific impulse of liquid oxygen with JP-4 and hydrazine is 265 and 280 seconds, respectively.

The things to remember about oxygen are as follows: (a) it must be kept in well-insulated storage tanks in order to maintain it below its boiling point, (b) it is easily produced, (c) it is a cheap material, and (d) a great deal is known about using it and handling it.

2. Nitric Acid.

Although liquid oxygen is a very good oxidizer, it is impossible to keep it in a tactical missile for 6 months or a year. Therefore, we are left with either nitric acid or hydrogen peroxide. Of the two, fuming nitric acid has received the most consideration for tactical missiles. Although nitric acid corrodes everything, burns poorly with JP-4, has only moderate performance with aniline, and is highly toxic, it remains the only oxidizer that has been stored satisfactorily for long periods of time. Although nobody likes to handle nitric acid, it has been quite satisfactory as an oxidizer.

The fuming nitric acids that have been considered for propellants are white fuming nitric acid, red fuming nitric acid, and mixed acid. The ordinary concentrated nitric acid familiar to high school chemistry students is about 68 percent nitric acid and 32 percent water. For propellant applications, we do not like to give this water a free ride; so we have to have something that has quite a bit more nitric acid in it. The first thing that was considered was a white fuming acid which contains approximately 97 1/2 percent nitric acid and 2 1/2 percent water. Red fuming acid contains from 83 to 85 percent nitric acid, from 13 to 15 percent NO₂ (nitrogen dioxide), and 2 percent water. Performance-wise, there is not too much difference between the white acid and the red acid. Corrosion-wise, white fuming acid is better than the red. White fuming nitric acid, however, develops sizable pressures under storage conditions

S-E-C-R-E-T

S-E-C-R-E-T

(of about 1,000 pounds per square inch). The only way found to date to get around the storage pressure problem is to add something to the nitric acid. If 13 to 15 percent NO_2 and 2 percent water are added to the acid, one gets the minimum pressures that are possible with this ternary system. These pressures run between 80 and 100 psia at 160°F and sufficiently low for storage in ordinary low-pressure containers.

This still leaves the corrosion problem. As mentioned before, the white fuming acid was found to be slightly less corrosive than the red fuming acid. Since both of them are very corrosive, considerable work was done toward developing corrosion inhibitors. Hydrofluoric acid was discovered to be a reasonably successful corrosion inhibitor. It is added in quantities of $\frac{1}{2}$ to 1 percent. Once the corrosion problem is alleviated, it is possible to return to the decomposition problem. There one finds that by using the hydrofluoric acid additive with the red fuming nitric acid, it is possible to produce a usable and storable acid. I might point out that, even though this corrosion inhibitor is reasonably good, there are still some sludging problems, and work is continuing toward developing better corrosion inhibitors.

Another problem with hydrofluoric acid as an inhibitor is that it precludes the use of titanium as the material of construction. There is still interest in using titanium to handle nitric acid, although there have been some violent explosions with titanium and red acid. At the present time the Jet Propulsion Laboratory is doing fundamental studies on the red acid - titanium system, and if they are able to determine the mechanism of these explosions and can control them, there will be renewed interest in the use of titanium with red acid. Such results would necessitate development of an inhibitor other than hydrofluoric acid.

Another acid that was considered at one time was mixed acid. It contains 88 percent nitric acid and 12 percent concentrated sulfuric acid. However, the problem of sludge formation (formation of insoluble iron and aluminum sulfates) virtually eliminated this acid from further consideration.

Fuming nitric acids are cheap, medium-performance oxidizers that can be stored for relatively long periods of time and at the same

S-E-C-R-E-T

time have fairly good physical properties. Red fuming acid has a freezing point around minus 70°F and white fuming acid around 43 to 47°F. The boiling point is about 140°F for the red fuming acid and 183°F for white acid. These freezing points and boiling points meet military specifications. The density is 1.6 g/cu cm, which is quite high. This means a high density impulse with nitric acid mixtures. I would mention again the decomposition pressure of less than 100 psia's at 160°F for the red acid. The viscosities of both red and white acids are satisfactory.

Performancewise the fuming acids are intermediate. They are not super-performance oxidizers but are good medium-performance oxidizers.

Nitric acid - aniline has a specific impulse of about 240 lb-sec/lb, and with hydrazine it will jump to about 257 lb-sec/lb. Nitric acid systems range around 250 lb-sec/lb, indicating strictly medium-performance systems. The density impulses, however, run over 300, which is very good when one considers these systems on a volume basis. Red acid gives a specific impulse of about 240 lb-sec/lb with JP-4, whereas the hydrogen peroxide - JP-4 system yields a value of 248 lb-sec/lb. The JP-4 fuels show a specific impulse of approximately 260 lb-sec/lb with liquid oxygen. This increase does not seem very large, but when it is considered in the range equation, it shows an appreciable increase in range, since range is a function of $(I_{sp})^2$.

The nitric acid - JP-4 system would be a very desirable system if it could be made to burn properly, since JP-4 is carried aboard most aircraft. There has been considerable combustion instability with these systems, however, and much work has been done and still is going on toward developing suitable additives to improve the combustion characteristics of these systems.

For handling inhibited nitric acids, aluminum alloys and 347 stainless steel are satisfactory. Teflon and Kel-F are nonmetallic materials suitable for contact with fuming nitric acids. The acids are not compatible with any organic materials or petroleum products. Fused silica, high-chromium and high-silicon irons and stainless steels, ceramic materials, and Duriron are used in the production of nitric acid.

A few miscellaneous properties of nitric acid are of interest. Nitric acid is insensitive to shock, which makes it desirable from a handling point of view. Although it must be shipped as a corrosive

S-E-C-R-E-T

liquid, it can be shipped in carboys, drums, tank cars, or trailers. It is quite toxic, since the fumes contain large quantities of nitrogen dioxide, which is an extremely toxic gas. If one is in an area where there are large quantities of nitrogen dioxide, an independent oxygen supply is essential because ordinary gas masks do not give adequate protection. Nitrogen dioxide does give a warning by its reddish brown color, so that, when these fumes are noticed, persons can be cleared from the area. It has this advantage over hydrogen peroxide and some of the other oxidizers and fuels that are sensitive to thermal shock or mechanical shock.

Nitric acid is produced by the catalytic oxidation of ammonia. Air and ammonia are reacted at 750°C and at 100 lbs per square inch pressure with a platinum catalyst to produce the NO₂ which is then dissolved in water. This process yields 60 to 65 percent acid, the ordinary concentrated acid of commerce. This acid is then distilled with sulfuric acid to give nitric acid concentrations of 95 to 97 percent. The red fuming acid is made by dissolving NO₂ in concentrated nitric acid. The actual process variables for the production of red acid have not been published. In 1955 there were more than 2 million tons of anhydrous nitric acid equivalent produced, which indicates a very adequate supply. Obviously, there are many producers. Most of these production facilities could be converted to red fuming acid production in an emergency. The General Chemical Company,* Hercules,** and Du Pont are the major producers of red acid for the armed forces. Cost is below 10 cents per pound in drum lots, with the inhibited acid slightly higher. The inhibited red fuming nitric acid is the acid of the rocket trade at the present time.

Organizations that are interested in nitric acid and have further information on this subject are the Wright Air Development Center; Wright-Patterson Air Force Base and Army Ordnance; Office of the Chief of Ordnance, Washington, D.C.; Redstone Arsenal, Huntsville, Alabama; and the Jet Propulsion Laboratory at the California Institute of Technology, Pasadena, California. Nitric acid has been of most interest to the Air Force and the Army, since it poses problems of shipboard handling to the Navy because of the toxic nitrogen dioxide fumes that are given off. Companies that have been engaged in development work with nitric acid as oxidizers are Aerojet-General Corporation; Reaction Motors, Inc.; and Bell Aircraft Co.

* General Chemical Division of Allied Chemical and Dye Corporation.

** Hercules Powder Company, Inc.

S-E-C-R-E-T

3. Nitrogen Dioxide.

In addition to the fuming acids, there has been some consideration of nitrogen dioxide as a rocket oxidizer. It has a fairly good performance, although not quite as high as nitric acid. Nitrogen dioxide, however, has a relatively high freezing point (12°F), which makes it unsuitable for military applications. Some work has been done on decreasing the freezing point by the use of additives. The most successful additive so far has been nitric oxide (NO), another oxide of nitrogen. A system containing 30 percent nitric oxide and 70 percent nitrogen dioxide has a freezing point of minus 110°F. This system develops storage pressures of about 300 psia at 160°F. Although it is not sensitive to shock, it is very toxic, and extreme care must be taken in handling it. It must be shipped in steel cylinders as a Class A poison. No pressure release valves are permitted. It is noncorrosive in the dry state. However, if a little moisture is present, it becomes quite corrosive. Nitrogen dioxide is in one of the intermediate steps in the nitric acid production process.

4. Mixed Acid.

Mixed acid contains 88 percent nitric acid and 12 percent sulfuric acid. Its density is about 1.7 g/cu cm, and its freezing point is approximately minus 60°F. It has a lower performance than either of the fuming nitric acids, and, in addition, there is a problem of sludge formation. If this problem could be solved, perhaps the Navy would be interested in mixed acid for shipboard application.

5. Ozone.

Ozone is another form of oxygen, having the molecular formula O_3 rather than O_2 . Our interest in ozone stems mainly from its somewhat improved performance characteristics and its considerably improved density. Its density is about 1.6 g/cu cm compared with about 1.1 g/cu cm for liquid oxygen. Therefore, less volume is required to package it. The improvement in performance, say with JP-4 (jet fuel), is measurable. Liquid oxygen with JP-4 would have a specific impulse of about 265, while 100 percent ozone with JP-4 -- if we knew how to use a 100 percent ozone -- would be about 280. There is not a lot of improvement in performance, but the improvement in density seems to make its consideration worthwhile.

S-E-C-R-E-T

The stability of ozone presents the greatest problem in its use. Extremely clean containers and ideal conditions are still not sufficient to prevent its decomposition. The only way that it has been used thus far in tests is in combination with liquid oxygen. Concentrations of about 20 to 25 percent ozone have proved possible. Considerable research activity is going into the problem of stabilizing ozone so that it can be used as a rocket oxidizer. It is extremely dangerous to handle, it is explosive, and it is somewhat toxic. It is, however, compatible with certain materials, such as aluminum, glass, stainless steel, Teflon, Kel-F, and polyethylene.

Ozone is produced by an electric discharge in an oxygen atmosphere, and its purity depend on the purity of the oxygen used as the raw material. Its impurity is, of course, oxygen. The potential production capacity of ozone is unknown because of the many uncertainties in handling it. Sources of information for ozone would include: Armour Research Foundation, Wellsbach Corporation, Linde, Air Reduction, and Olin Mathieson. Some research work has been done at Princeton University. The Western Development Division and the Wright Air Development Center have both sponsored small research projects on ozone.

6. Fluorine, Perchloryl Fluoride, and Chlorine Trifluoride.

I am going to talk briefly about the role of fluorine and its compounds as oxidizers. I will consider three compounds here: fluorine itself, chlorine trifluoride, and perchloryl fluoride. Perhaps the most outstanding feature of these three compounds is their densities, which are 1.11, 1.77, and 1.41 g/cu cm, respectively. The freezing point and boiling point characteristics of fluorine itself are about the same as for oxygen, so that the same storage and handling problems exist. As one forms compounds involving fluorine, these characteristics tend to become more moderate. Except for fluorine itself, the densities tend to be rather high, and this has the usual favorable implication as far as the density impulse is concerned.

Fluorine is one of nature's anomalies, in a sense. Some of its compounds are very highly reactive -- among the most reactive that we know of -- while others, such as the hydrocarbon analogs involving fluorine, tend to be just the opposite and very unreactive. Consequently, fluorine plays a very large role in the picture of rocketry -- in one case

S-E-C-R-E-T

S-E-C-R-E-T

the reactive materials as oxidizers; in the other case the inert materials as lubricants, gaskets, and coatings. Fluorine itself shows the highest performance of the chemical oxidizers both with respect to its impulse and with respect to its density impulse. It is extremely corrosive, extremely reactive, and very toxic.

Another important feature of fluorine is its limited availability. The world's resources of fluorine are low, and only a portion of those resources can be used for rocket purposes. This further limits its use. It is handled similarly to oxygen and requires the same type of refrigeration and insulation. It is normally produced as a 98 percent pure material. Its boiling point is minus 306°F, its freezing point minus 360°F. The spread is rather narrow, but there is no need to worry about its freezing.

I have some performance figures here in comparison to liquid oxygen. If we take hydrazine and hydrogen as fuels and fluorine as the oxidizer, we find that hydrazine has an impulse of 315 seconds and hydrogen 342 seconds, whereas, if liquid oxygen is used, the impulses are 270 and 315, respectively. So you see that it runs 10 percent or better above the liquid oxygen figures. When comparing the density impulses, fluorine looks even better because it has higher density.

Experimentally, fluorine systems have been fired at the 5,000-pound thrust level, and very high efficiencies have been obtained, up to 95 percent of theoretical performance. Work is now being done on the fluorine-ammonia system at a much larger scale -- the 35,000-pound thrust level.

Since fluorine is so corrosive, there is a major problem of materials of construction for handling it. For example, things like glass and concrete materials, if placed in a jet of hot fluorine, will react violently. These are materials that we normally consider as being rather inert. Fluorine reacts with practically all the metals when hot. It is extremely toxic, on about the order of phosgene, and, perhaps more to the point, the exhaust product that one typically gets when using fluorine as an oxidizer, hydrogen fluoride, is also quite toxic. In experimental work, special measures have to be taken to try and render harmless the exhaust products because of the safety of the workers in the vicinity. Aluminum alloys, particularly 61 ST alloy and type 356

S-E-C-R-E-T

cast aluminum, can be used for handling liquid fluorine. Stainless steel, bronze, and brass also have applications where service life can be short. These materials will not stand up over protracted periods. In some cases, by treating the mechanical system carefully, you can achieve a coating of the metal by a relatively inert fluoride layer, and, apparently, success in the use of any of these materials may depend on that layer, its existence, and its remaining intact. Metal surfaces must be free of organic matter, as in the case of oxygen. Metallic tin has been used for labyrinth-type seals. A titanium carbide material is an example of a cermet that has application. Silver can be used in some cases. Materials such as Teflon and Kel-F have some application.

Fluorine is made from hydrogen fluoride, electrolytically. The cost of the hydrogen fluoride used in the manufacture of fluorine is about \$0.20 a pound, so that you can look for a cost of fluorine on the order of \$0.50 to \$2.00 a pound.

As far as fluorine is concerned, there are a number of companies that have been interested and have technical knowledge, including Du Pont, General Chemical Co., Hooker Electrochemical Co., Harshaw Chemical Co., Union Carbide Nuclear Co., and Pennsalt Manufacturing Co. Work with fluorine is presently being sponsored by the Wright Air Development Center, at North American Rocketdyne, and by Bell Aircraft. Presumably, further information on the current developments could be obtained there.

Fluorine can be used in mixture with oxygen, and in these cases, of course, with physical properties and performance that are somewhere between the performance for the pure materials. Chlorine trifluoride is about as reactive as fluorine. It has a much higher density, and it is much more manageable in the sense that it has lower vapor pressures and a higher boiling point. The same problems of toxicity exist, but it is somewhat better in its chemical reactivity and corrosion aspects. Chlorine trifluoride with ammonia gives a specific impulse of 246, compared with 310 for fluorine with ammonia.

One of the reasons why these fluorine compounds give such high density impulse performance is that we utilize much higher ratios of oxidizer to fuel than is possible, say, in the case of liquid oxygen.

S-E-C-R-E-T

And with a material that has a high density, of course, this becomes an advantage where the oxidizer is present in larger quantities.

Chlorine trifluoride can be handled in mild steel at ambient temperatures, but not at elevated temperatures. Iron, nickel, and Monel have been used.

Chlorine trifluoride is made by the direct reaction of chlorine and fluorine and is subject to the same limitations as fluorine as far as the availability of raw materials is concerned. Pennsalt Manufacturing can supply this in experimental quantities and probably is also the best source of information.

The third and final of the fluorine compounds, perchloryl fluoride, is a fairly new development. It has the molecular formula FClO_3 . It has the relatively high performance characteristic of the fluorine compounds, and it is much less reactive as far as corrosion and handling are concerned. It also has a higher boiling point than liquid oxygen. At the moment, the estimated cost of this material is on the order of \$30.00 a pound, so that you can realize the stage of its development. It is handled as the anhydrous material. I do not have any information on the means of synthesis, although it does involve an electrolytic process utilizing sodium chlorate and hydrogen fluoride. Performancewise, perchloryl fluoride with unsymmetrical dimethylhydrazine has a calculated impulse of about 270, while unsymmetrical dimethylhydrazine with liquid oxygen has a calculated impulse of 277. From these figures it becomes apparent that this might be competitive with oxygen as far as impulse is concerned. It is still in the research stage of development, and the work that we know of is being done at Naval Air Rocket Test Station. From the production point of view, Pennsalt is a participant.

7. Tetranitromethane.

The last oxidizer which we will consider is tetranitromethane. This is a compound that has 1 carbon with 4 nitro groups attached to it, and, as might be expected, this would be unstable and fairly explosive. The material has a freezing point of about 57°F , which is the highest of any of the oxidizers that we have considered, and from this point of view it is the least desirable. It has a density of about 1.64 g/cu cm, which makes it one of the

S-E-C-R-E-T

highest in this desirable property. As far as safety is concerned, its big drawback is that it is sensitive to heat and to thermal and mechanical shock. Another disadvantage with tetranitromethane is its fairly low production rate in this country, or anywhere, for that matter. Production now is practically zero. The price for this material has been estimated at \$20.00 per pound. Conceivably it can be produced from about \$0.25 to \$1.00 a pound.

It is interesting that during World War II Germany was considering tetranitromethane as a material to use in the V-2, but, after a laboratory was destroyed by an explosion, the Germans decided to use oxygen instead.

There are several ways by which tetranitromethane can be produced. They all involve nitric acid as a nitrating agent. Raw materials in the system can be acetone, acetic anhydride, or ethylene, and these materials are all fairly common. Acetic anhydride is probably less common, but certainly acetone and ethylene are available in large quantities.

One other interesting thing about this material is that it is a byproduct in the production of TNT. In the usual methods of producing TNT a sulfide wash is employed to destroy the tetranitromethane which has been formed. It is formed in small quantities, but apparently it makes the TNT even more sensitive than it normally is.

Hefco Chemicals and Pennsalt produce tetranitromethane and are probable sources for more information. A good general bibliography on this particular compound has been compiled by the Hazeltine Laboratory.

8. Summary of Oxidizers.

In summary, refer again to the list of the materials shown in Figure 14. I might point out again that the freezing points range quite considerably, as do the boiling points; that these oxidizers contain either oxygen or fluorine (either the elemental material or in compounds); and, as previously mentioned, that two of these oxidizers are operational. These are liquid oxygen and nitric acid. Liquid oxygen is cheap, available, and easy to handle but has a low density and a problem of storage. In fact, liquid oxygen is usually considered for use

- 30 -

S-E-C-R-E-T

S-E-C-R-E-T

in a ballistic missile rather than in a tactical missile or in an anti-aircraft missile. Nitric acid is also a cheap, available material, but it presents a corrosion problem, especially in long-time storage.

Hydrogen peroxide has a high melting point problem, but it is noncorrosive and fairly nontoxic. If the problem of long-time storage could be solved, it would perhaps become accepted as one of the operational oxidizers. The Navy is beginning to use hydrogen peroxide as an oxidizer.

The research-stage oxidizers are ozone, fluorine, perchlorylfluoride, chlorine trifluoride, and tetranitromethane. Characteristically, they have a rather high cost and fairly low production.

The following tabulation summarizes the specific impulses of the oxidizers with JP-4 and hydrazine:

<u>Oxidizer</u>	<u>I_s with JP-4 (lb-sec/lb)</u>	<u>I_s with Hydrazine (lb-sec/lb)</u>
Chlorine trifluoride		250
Nitric acid	240	260
Tetranitromethane		260
Hydrogen peroxide	250	265
Liquid oxygen	265	280
Ozone	280	
Fluorine	280	320

You will notice that the two materials which are operational do not give the highest performance. They are still fairly high, however, when compared with monopropellants. With hydrazine the materials have a specific impulse which ranges

S-E-C-R-E-T

approximately 10 percent higher than with JP-4. There is a great deal of interest in fluorine as an oxidizer and considerable current interest in the fluorine-ammonia system.

B. Fuels.

It has been previously pointed out that with oxidizers use is made primarily of compounds containing either oxygen or fluorine because both are low-molecular-weight elements which are oxidizing in nature. There is one element which is contained in almost all fuels. This is hydrogen. Hydrogen is beneficial in lowering the average molecular weight of the exhaust products. As the molecular formula for each fuel is discussed, therefore, note that each usually contains large fractions of hydrogen in the molecule. The choice of fuels is much larger than the choice of oxidizers. A number of organic materials are applicable. Of course, the most common organic materials which are available and used as fuels are those derived from petroleum. Jet fuel, kerosene, and gasoline are good examples. There are also some inorganic materials such as ammonia and hydrazine which contain large amounts of hydrogen and thus make good fuels.

Figure 15 lists most of the fuels which seem to be of fair importance today such as ammonia, aniline, ethyl alcohol, liquid hydrogen, hydrazine, JP-4, and UDMH. JP-4 is a particular specification of jet fuel, and UDMH is unsymmetrical dimethylhydrazine.

1. Aniline.

By all our previous criteria, aniline does not really seem to be a good fuel. It has a freezing point which is only slightly below that of water. It does not have a high specific impulse, being only about 220 with red fuming nitric acid. But there is one characteristic of this particular system, aniline - red fuming nitric acid, that is all-important. The two components are spontaneously combustible. In other words, by adding nitric acid to aniline in a motor, sufficient energy is produced -- and rapidly -- so that combustion is initiated immediately. In addition, nitric acid and aniline compose a storable system. These are the main reasons for this particular system being used. Nitric acid and a mixture of aniline and other components are being used in the Corporal, a missile developed at the California

S-E-C-R-E-T

Institute of Technology. The acid-aniline system was originally developed at the California Institute of Technology and was in use as early as 1943.

Some characteristics of aniline are of interest. It is relatively inexpensive. Aniline has a high freezing point and is somewhat toxic. The skin must be protected, and there are inhalation toxicity difficulties at times. Aniline is relatively stable and can be shipped in a mild steel or glass container. It has a solvent action on most greases and lubricants as well as on some plastics, so that the packing problem is sometimes difficult.

Aniline is produced by reaction of nitrobenzene in an iron vessel or by the reaction of chloral benzene with ammonia. Cost is about 20 to 22 cents a pound. Some of the manufacturers are Calco Chemical Division, American Cyanamid Co.; National Aniline Division, Allied Chemical and Dye Corporation; Du Pont; and US Rubber Co. There also is some interest in the use of the acid-aniline system on the part of the people at Redstone.

In an effort to decrease the freezing point of aniline, some materials have been tried as additives. Propyl alcohol, which lowers the freezing point to about 0°F, helps somewhat. There is no appreciable effect on performance, which, of course, is already low. The mixture which is used in the Corporal is 46 $\frac{1}{2}$ percent aniline, 46 $\frac{1}{2}$ percent propyl alcohol, and 7 percent hydrazine.

Another early development which was tried in an effort to eliminate the freezing-point problem was the use of monoethyl aniline. Its freezing point is quite low, minus 82°F. The performance of monoethyl aniline with nitric acid is about the same as that of aniline. No use of monoethyl aniline is currently being made.

2. Ethyl Alcohol.

Ethyl alcohol is a compound with which most of us have some familiarity. It is common material and is produced in this country and throughout the world in large quantities. It has a freezing point of minus 174°F and a boiling point of 173°F. This makes it a very convenient compound to use operationally, because it has a wide liquid range. Its density is a little low, 0.8 g/cu cm, compared

S-E-C-R-E-T

with some of the oxidizers, which were all greater than 1 g/cu cm. Ethyl alcohol does present somewhat of a fire hazard. There is no particular corrosion problem. Steel and glass are adequate for handling and producing ethyl alcohol.

Ethyl alcohol is produced primarily by two methods. The time-honored fermentation process followed by a simple distillation can produce 95 percent ethyl alcohol. By using a more sophisticated distillation, 100 percent alcohol can be produced. The second and perhaps more modern way of producing ethyl alcohol is from ethylene and water via a catalytic process. Literally, a water molecule is attached to an ethylene molecule, and ethyl alcohol results.

The two processes, as far as cost is concerned, are competitive. For example, in 1950, 80 million proof gallons were made by fermentation processes, and 100 million gallons were made from ethylene, which is a derivative of petroleum.

I might mention that in the fermentation process almost any carbohydrate can be used as a raw material. The materials most commonly used are grains and molasses. In fact, the price of molasses just about dictates the price of fermentation alcohol in this country. Molasses is imported from Cuba primarily. The cost of 190-proof alcohol is about 40 cents per gallon, while 200-proof alcohol (100 percent alcohol) ranges between 48 cents and 61 cents per gallon. Major producers include most chemical and oil companies including specifically Du Pont, Dow, Union Carbide and Carbon, Commercial Solvents, Celanese, Olin Mathieson, US Industrial Chemicals, and Shell Chemical.

Special considerations with the use of ethyl alcohol are its potability and its control by the internal revenue department. These factors have discouraged its use by the armed services in the past.

Our interest in ethyl alcohol is because it is cheap and partially because it was used successfully by the Germans in the V-2. We have a lot of experience with it, and we know it works. The Germans made it work quite well, but the Germans did not use absolutely pure ethyl alcohol. They used a mixture of 75 percent ethyl alcohol - 25 percent water. They put water in it because of a problem of cooling the rocket motor. They found the addition of 25 percent water to their

S-E-C-R-E-T

fuel resulted in a decrease in the temperature of the rocket motor which increased the life of the motors. This addition does not alter the freezing point or the boiling point very much but increases the density slightly. The specific impulse is not greatly affected.

The specific impulse with ethyl alcohol and oxygen is about 240 -- slightly lower than some of the systems we talked about, such as with hydrazine and JP-4, but not intolerably so.

3. Petroleum Fractions.

This is a rather large topic to cover here, and I am going to do it briefly. The significant thing about petroleum products as rocket fuels is their availability. You might say that compared with most of the other fuels, petroleum products are unlimited. We have to remember at the same time that rockets will be competing for these materials with practically everything else that moves. Four principal fuels are JP-4, JP-5, JP-X, and kerosene. They are all complex mixtures of various types of hydrocarbons and are quite similar in their physical and chemical properties, with the exception of JP-X, which has a substantial amount of additive in it. These fuels have densities that are low compared with the densities that were mentioned in our discussions of oxidizers, ranging from 0.75 to 0.80 g/cu cm. Viscosities are favorable. They have the problem of their inflammability and the explosive vapors that are generated in air atmospheres. These may require special techniques for handling and ventilation. The JP-4 is a broad hydrocarbon cut; the JP-5 is a somewhat narrower cut in a higher temperature boiling range.

The JP-X is a mixture of JP-4 (60 percent) and UDMH (40 percent). Specific impulses do not vary widely among the various hydrocarbon fuels. For the JP-4, we have a specific impulse of 240 with red fuming nitric acid, 265 with liquid oxygen, and 280 with fluorine. The density impulse is 260 with liquid oxygen, 310 with red fuming nitric acid, and 340 with fluorine, with the principal advantage coming from fluorine.

There is a problem with JP-4, and it was this problem that led to JP-X, in a sense. It is difficult to ignite, and it shows a high degree of combustion instability with nitric acid. Both of these

- 35 -

S-E-C-R-E-T

S-E-C-R-E-T

topics have been the subject of extensive investigations by Reaction Motors, Aerojet-General, and others. The addition of 40 percent unsymmetrical dimethylhydrazine to JP-4 was made with the hope that combustion stability would be improved, that ignition delay would be reduced, and that, in general, it would perform more satisfactorily, and this is the case. There is still a tendency to consider JP-X as a petroleum fuel, but the 40 percent of UDMH puts it pretty well over into the field of a synthetic chemical fuel. Problems of cost, availability, and so on connected with UDMH might be fairly serious. JP-5, because of its higher flash point and higher boiling point range, is particularly suitable for shipboard use, and that is where it is primarily used. The Army is using a mixture of JP-4 and UDMH which is different from the JP-X mixture -- 83 percent JP-4 and 17 percent UDMH in the Nike missile.

As far as handling is concerned, these petroleum materials are quite stable. They do tend to form gums on standing, especially if exposed to elevated temperatures or an oxidizing atmosphere. They can be made either directly as a straight-run virgin product, or they can be made by the usual refinery techniques of cracking. The cracked materials are less stable.

There are no particular problems with storage or shipping. The Interstate Commerce Commission has adequate regulations covering these materials. Construction materials that are compatible include most of the common ones -- steel, black iron, tin, magnesium, and aluminum. One must be a bit careful about the sulfur content of some of these fuels. It can cause corrosion problems under some conditions. The specifications, if I recall correctly, however, are pretty low in sulfur. The principal problem in storing and handling these materials is the explosive nature of the vapors. They are also to some extent toxic, but this is not as serious as the explosion hazard.

I think all I need to say about the production of these materials is that most any refinery can produce them in direct proportion to the amount of crude which they have to process. These materials can be made at the sacrifice of other products that are turned out by a refinery. Perhaps the ideal situation would be to have one petroleum hydrocarbon fuel that could be used for every conceivable purpose. But we are not quite to that point yet; so we still have to

- 36 -

S-E-C-R-E-T

S-E-C-R-E-T

consider such things as aviation gasoline, motor gasoline, lubricants, and diesel fuels in competition with the rocket fuel. As far as information is concerned, there has been much published on these materials. Physical data can be obtained from any refinery and from many reports that are in the hands of the military.

Performance of these fuels has been measured by North American, the Wright Air Development Center, and the Navy. JP-X has been worked on by Aerojet and WADC.

There is one additional topic which may be a little bit novel. That is the production of slurries, wherein the fluid is JP-4, for example, and the solid materials suspended may be metallic. Work has been done by Reaction Motors, Aerojet, and M.W. Kellogg. Slurries of metal powders suspended in hydrocarbon fuels have been considered and have been tested with the objective of increasing range or thrust and getting superior combination characteristics. Some of the metals that have been used are aluminum, boron, and magnesium. Aluminum was eliminated finally because of its tendency to form a molten exhaust product, aluminum oxide, which would coat the parts of the motor. Boron gave indication of providing increased range. I want to distinguish here between boron slurry in a hydrocarbon and boron fuels, which will be discussed later. Magnesium did not increase range particularly, but it did increase the thrust.

The major problem with metallic slurries is the difficulty of stabilizing the suspension. The metal particles tend to separate out in long storage. There must be some means provided for resuspending them from time to time, especially just prior to use. Surface-active agents have been added in an attempt to improve the suspensions. Other problems that are always attendant in handling slurries through pumps and valves exist here also, such as erosiveness, tendency to clog, and so on.

The magnesium slurries that were tested had a higher reactivity, higher thrust potential, and higher impulse characteristics per unit volume of the slurry. This would make them valuable, for example, in after-burners, where maximum thrust is required for take-off. The 50-50 magnesium - JP-4 slurry is the result of a compromise between handling and preparation characteristics and combustion characteristics. Not only have hydrocarbon fuels been used in investigating slurries, but other fuels as well, such as aluminum and JP-4, aluminum and ethylene oxide, beryllium and nitromethane, boron and nitromethane, boron and JP-4, boron hydrides and JP-4, and magnesium and JP-4.

- 37 -

S-E-C-R-E-T

S-E-C-R-E-T

4. Unsymmetrical Dimethyl Hydrazine (UDMH).

Hydrazine has been previously discussed as a monopropellant and as a fuel used with an oxidizer in bipropellant systems. In bi-propellant systems, however, it is beginning to be superseded by UDMH, a fairly recent development.

Figure 15 shows a comparison of some properties of UDMH and hydrazine. The main difference is in the freezing point, minus 72°F for UDMH and 35°F for hydrazine, an obvious advantage for UDMH. Figure 15 shows that the density of hydrazine is higher than that of UDMH. So there might be certain cases where hydrazine would be used in preference to UDMH. For most operational uses, however, UDMH would be superior because of its lower freezing point. The viscosity is higher, but this is still well within the usable range.

Performancewise, UDMH is about 1 to 2 percent lower with most oxidizers than is hydrazine. Its density is reasonably high, and its storage properties are good. It is used as an additive with JP-4, and it has excellent combustion properties. UDMH is hypergolic with nitric acid and might replace aniline, which is used with nitric acid primarily because of its hypergolicity. UDMH with white fuming nitric acid has a specific impulse slightly over 240 compared with about 220 for aniline.

UDMH is flammable and fairly toxic. It is insensitive to shock but should be stored below about 120°F. Most common materials, iron and steel, nickel and aluminum, are satisfactory for use with UDMH. Among the plastics, Teflon, polyethylene, asbestos, glass, and wood are used. Rubber and neoprene are not recommended.

The production method is unknown to us, but at the present time it is available in the range of price of about \$4.00 to \$6.00 per pound from Olin Mathieson, Aerojet-General, and Metalectro. Both North American and Aerojet-General have done important rocket development work using UDMH.

A rather recent development is the use of a mixture of UDMH with diethylene triamine (DETA). The mixture of 60 weight percent UDMH - 40 weight percent DETA has been proposed as an alternative

S-E-C-R-E-T

S-E-C-R-E-T

to ethyl alcohol - water mixtures. This particular mixture has about the same density as ethyl alcohol - water mixtures and yet gives about about 20 percent higher performance than does ethyl alcohol with liquid oxygen. Its specific impulse with liquid oxygen is about 275, while that of ethyl alcohol is of the order of 240.

There are other advantages besides performance. The mixture is somewhat less toxic than UDMH. Also, DETA is much cheaper than UDMH, so that the mixture, of course, would be cheaper as well. Information sources on this mixture are Westvaco and North American.

5. Ammonia.

Ammonia is a very important industrial chemical and is available in large quantities. It has one great disadvantage as far as rocket fuels are concerned in that its boiling point is minus 28°F. In other words, it has to be handled in much the same way as liquid oxygen or liquid fluorine. It has a fairly low density, 0.7 g/cu cm, but it has some advantages, one of which is that it is stable. The toxicity problem of ammonia is not too great. It is toxic, but it is detectable at concentrations considerably below the limit at which it becomes toxic. The human nose is a reliable detector in this case.

One of the characteristics of ammonia is its solubility behavior. It is extremely soluble in water. Among the more common gases it is the most soluble, about 30 percent, at normal pressure and temperature. It is also a good solvent. It will dissolve materials like sodium, potassium, calcium, and lithium. I mention these metals because these materials themselves (sodium, potassium, lithium) are potential high-energy fuels. But they are metals, and when dissolved in ammonia a liquid system is obtained. In fact, there has been a lot of work done in the past with these particular metals.

Corrosion is not much of a problem with ammonia. The materials which should be avoided are copper and tin, because ammonia will dissolve them. Normal steel and glass are perfectly acceptable to use with ammonia.

Ammonia is made commercially by the classic Haber process. This is a high-pressure catalytic reaction between nitrogen and hydrogen.

S-E-C-R-E-T

This process was developed in Germany prior to World War I and supplied Germany with a source of nitrates for World War I. In fact, many people say that without the Haber process World War I would not have been fought. In effect, this process has made every country in the world independent of Chilean nitrate, an important economic, as well as military, fact. The problem is not so much one of a method to produce it as one of getting raw materials. Hydrogen is available in large quantities. It can be produced from carbon monoxide and water by a catalytic process. That is probably the way most of the hydrogen is made for ammonia synthesis. Nitrogen is produced from the air. Both raw materials are fairly cheap and are readily available. The production in this country amounted to approximately 4 million tons last year, which makes it one of our largest chemicals.

A number of companies have recently built ammonia plants to fulfill the demand for liquid ammonia as a fertilizer. Almost every chemical and oil company produces liquid ammonia. Oil companies became interested because they have a great deal of hydrogen left after their refining operations.

Ammonia plays an especially important role in the rocket fuel program because the commercial process for nitric acid uses ammonia as a principal raw material. Almost all nitric acid is made by the catalytic oxidation of ammonia. Therefore, nitric acid production is tied to ammonia production.

As previously mentioned, an important disadvantage of hydrazine is its high freezing point. Since ammonia is similar to hydrazine and, in addition, has a lower freezing point, the two should make a good combination. An attempt was made to produce a composite fuel of these two, but the result was not too satisfactory. The melting point can be lowered to about minus 30°F with such mixtures. However, the boiling point is lowered to a point between zero and 70°F. The addition of ammonia to hydrazine does not particularly extend the liquid range but does lower it. The specific impulse for this system is of the order of 260 to 270 sec depending on the oxidizer used.

S-E-C-R-E-T

6. Boron Compounds.

The next class of compounds to be discussed is the boron compounds, three groups of which have been considered for rocket fuels. These are the boranes, their organic derivatives, and their metal derivatives. The boranes are compounds that are analogous to hydrocarbons, such as diborane, B_2H_6 ; tetraborane, B_4H_{10} ; pentaborane, B_5H_9 ; and hexaborane, B_6H_{10} . Their organic derivatives are compounds such as methyl borohydride, $CH_3B_2H_5$, while their metal derivatives contain compounds such as aluminum borohydride, $Al(BH_4)_3$, or lithium borohydride, $LiBH_4$. Conceivably as many as 100 boron compounds could be considered in these categories. Their melting points range all the way from minus $165^\circ F$ for B_2H_6 to $275^\circ F$ for lithium borohydride. The boiling points range from minus $92^\circ F$ to $213^\circ F$. A wide temperature range in which to select a compound is available. Densities are in the order of about 0.6 g/cu cm for this class.

Most of the interest centers about one or two of these compounds. Diborane, which perhaps has received the most interest, is a gas at room temperature and atmospheric pressure. It is important because it is the intermediate compound from which all the boron compounds are made.

The source of boron compounds is borates, most of which are located in California. The ores contain primarily sodium borates and calcium borates, in the form of borax, kernite, colemanite, or ulexite. There are other sources of raw materials widely distributed throughout the world. The US is fortunate in that the California deposits are more concentrated than those of other countries. Europe has quantities of boron compounds.

In producing the desired boron compounds from the boron ores, certain materials are important intermediates, and these are, as they are encountered, boric acid, boron trifluoride, and diborane. The boron ores are treated with sulfuric acid to produce boric acid. The boric acid can be processed one of two ways to produce boron trifluoride, BF_3 , which is reacted with lithium hydride to produce diborane, B_2H_6 . The diborane is then converted into the desired compound through various processes which differ with the end product desired.

S-E-C-R-E-T

In the process route sketched above, the production of boric acid is quite simple, but a great deal of industrial know-how goes into the production of BF_3 . The problems encountered in its production are formidable, and any country would have difficulty in solving them. One of the two processes uses fluorosulfonic acid, which is not a readily available material. The other process uses calcium chloride to produce the boron trichloride. The lithium hydride required to produce diborane from BF_3 is an expensive material which takes a lot of power to produce. Most of our producers of lithium hydride are located near Niagara Falls. Three of the interesting end products which are produced from diborane are B_5H_9 , derivatives of B_5H_{11} , and aluminum borohydride. These liquid compounds are attracting considerable attention in this country.

The Department of Defense and its contractors are quite reluctant to discuss or release information about boron compounds, and consequently it is difficult to obtain information. If anyone has any further interest in this field, he can obtain information from the Bureau of Aeronautics upon demonstrating the proper need to know. Some of the research on the properties of these compounds is being conducted by the Naval Research Laboratory, the University of Chicago, the University of Pittsburgh, the Carnegie Institute of Technology, and the National Bureau of Standards.

One disadvantage of boron compounds is that they give solid decomposition products which are undesirable from a heat transfer point of view. As far as performance with liquid oxygen is concerned, the boron compounds have a specific impulse of about 310 sec compared with 275 sec hydrazine. In spite of high cost and inherent difficulties, their superior performance is the reason why boron compounds have been given so much attention.

7. Liquid Hydrogen.

We find in looking over a table of computed specific impulse values that liquid hydrogen is about the only propellant that comes close to meeting the ideal performance characteristics (specific impulse greater than 350 lb-sec/lb). It has a specific impulse of about 375 with fluorine. The density of liquid hydrogen, however, is approximately 0.07 g/cu cm, which is about one-twelfth that of water. Therefore, you are faced with a density impulse of less than 100, which means that you need exceedingly large tanks to handle the large volumes of hydrogen required.

- 42 -

S-E-C-R-E-T

S-E-C-R-E-T

I would like to make one more point as far as judging propellants is concerned. We have been talking about "specific impulse" and "density impulse" throughout our discussion. Although these are convenient methods for the chemist to use in evaluating a propellant, it is necessary for an accurate over-all evaluation to run a complete systems analysis for the particular mission that you wish to perform. In many cases the over-all cost will come out very close for a number of propellants ranging considerably in specific impulse, cost, and other factors.

There is some consideration at the present time of the use of liquid hydrogen for applications that are not volume-limited. One is the use of hydrogen in air-breathing engines for high-altitude aircraft. For altitudes of 100,000 feet or more, the airplane has to be very large in order to provide the required wing area; hence there is a large tank volume available. Since ordinary jet fuels will not burn at this altitude, there is some speculation that liquid hydrogen might find application in this area.

An estimated cost of \$10.00 to \$20.00 per pound was made by Aerojet in 1950. At that time Aerojet had a small plant producing about 90 liters per hour. There were a few other research organizations producing liquid hydrogen. The University of Chicago, the University of California, and Ohio State University produced liquid hydrogen on a research scale. There have been some estimates of \$0.30 to \$3.00 a pound for large-scale hydrogen. However, I think it is important to consider what Aerojet stated in 1949: "Considerable design and operating experience with new expansion engine cycles will be required before completely satisfactory high-capacity production plants can be built." At that time, Aerojet estimated that a 2,500-pound-per-month plant, still a relatively small plant, as far as rocket propellants go, would cost approximately \$100,000.

The organizations that have done the major portion of work with liquid hydrogen are the Herrick L. Johnston Enterprises, the Aerojet-General Corporation, the Ohio State University Cryogenic Laboratory, the University of California, and the University of Chicago.

Hydrogen has the disadvantage also of having explosive characteristics with air or oxygen, but the major disadvantage is its extremely low density. This is the penalty that you have to pay even though hydrogen systems have exceedingly high performance.

S-E-C-R-E-T

8. Summary of Fuels.

Aniline is an operational fuel with good storage characteristics, although it exhibits only moderate performance. Until very recently the 75 percent ethyl alcohol - 25 percent water system was considered for use in the Redstone missile, an intermediate-range ballistic missile system. As previously mentioned, there is a possibility that this system will be replaced with the UDMH-DETA mixture, which has essentially the same properties as the older alcohol-water mixture with the exception of a higher performance. Petroleum fractions are cheap and readily available. Hydrazine, because of its high freezing point, is receiving less and less consideration with the present development of UDMH. UDMH is increasing in popularity as a propellant, and to date it has been living up to expectations. Ammonia is of current interest as a high-energy fuel in the ammonia-fluorine system. It appears that people would prefer ozone to fluorine, but to date they have not been too successful in handling ozone. The ultimate choice between ozone and fluorine will depend on the outcome of research directed at controlling the ozone decomposition reaction. Considerable interest exists in boron compounds, although from the performance values previously mentioned it is evident that boron compounds are not the best rocket fuels. There is quite a bit of current interest in their applications to air-breathing engines. The Bureau of Aeronautics has sponsored a project jointly with Olin Mathieson and Callery Chemical Co. on the development of boron fuels. There is information available under the title Project ZIP if you have the proper clearance and need to know. High-performance liquid hydrogen is not being considered too actively at present.

IV. Summary.A. Chemicals.

I will summarize just briefly the picture as far as chemicals are concerned, and others here will take up materials in the sense that we have considered materials today. We have talked about roughly 20 to 25 different chemicals. Some of them are pure substances, some of them mixtures, and some complex mixtures. We have divided them into several groups: the monopropellants, the oxidizers, and the fuels, with about the same number of compounds in each category. In discussing their

- 44 -

S-E-C-R-E-T

S-E-C-R-E-T

sources, the raw materials from which they are made, the chemicals which go into the processes, and the manufacturing of propellants, we have named just about every major industrial chemical.

Now, what one does with all of these materials when it comes to a topic such as strategic control, I do not know. But it does point out the fact that you will have to look closely and look at everything, that there are no sources that can be overlooked, and that the information which you need to do a good job of control will be very detailed and will have to offer very broad coverage of the fields.

Some of the materials we have talked about are items of commerce today, and one might speculate that if we were to get into an all-out effort against an enemy in the near future, we would have to make use of these common materials. Many of the exotic materials are on the list here because we are still looking for the ideal material which will lend itself to the 5,000-mile range ballistic missile. This calls for the utmost in dependability in performance and dependability in storage because, as far as we know, if we ever use missiles of this type against an enemy, we would probably have to launch them on very short notice, which would mean having them in substantially a ready state.

We have talked about materials that cost from about a few cents a pound up to many dollars per pound. Here again, for conventional tactical use, we are interested in materials that have a reasonable price. But for this one big clincher that some of us are concerned about, cost is no object. I think that as far as chemicals are concerned, this pretty well sets the extremes.

I want to repeat that there is much, much more information that can be given in the areas that we have covered here today. It is a question of time to get it together and to analyze it. It is to be hoped that all of these compilations and analyses of information will be completed some day, so that we will have a current picture of where we stand and where we are going. The field of rocketry is a recent field and has not yet developed to the point where one would anticipate a high degree of stability.

- 45 -

S-E-C-R-E-T

S-E-C-R-E-T

B. Nonmetallic Materials.

The following list summarizes the nonmetallic materials that are compatible with various propellants:

Amine Mixtures.

Polyvinyl polymer plastics may be used.

Ammonia.

Ammonia is compatible with most materials that withstand the temperature of liquid ammonia; however, ammonia is not compatible with wood.

Aniline.

Koroseal, Vinylite, Teflon, and Tygon are compatible. Aniline exerts a solvent action on most greases and lubricants.

Boron Compounds.

Information may be available from the Navy Bureau of Aeronautics

Ethyl Alcohol.

Ethyl alcohol is compatible with most substances that are not oxidizers as well as with substances that are not affected by solvents.

Ethylene Oxide.

Nylon, Teflon, G.E. silicon rubbers, and glass are used. Molybdenum sulfide is used as a lubricant and thread compound. Kel-F is unsatisfactory.

Fluorine.

No good nonmetallics have been found except "cintanium" cermet (TiC-Ni), which is used for seals.

Hydrazine.

Polyvinyl chloride and polyisobutylene plastics, natural rubbers, and low-sulfur buna rubbers may be used.

- 46 -

S-E-C-R-E-T

5X1

S-E-C-R-E-T

Hydrogen.

Teflon valve seats, asbestos gaskets, and O-ring seals (if kept warm) may be used.

Hydrogen Peroxide.

Polyethylene, Kel-F, and polyvinyl chloride are suitable for gaskets. Fluorolubes, halocarbon oil, and perfluorolubes are used for lubricants.

Jet Fuel (JP-4).

Buna N rubber is compatible with JP-4.

JP-X (Jet Fuel - UDMH Mixtures).

Teflon and Butyl rubber may be used with JP-X.

Liquid Oxygen.

Ground mica powder, nonlubricated asbestos, unplasticized grades of Kel-F, Santa Susana sealer (fluorolube, molysulfide, and powdered lead), oxyseal, and water glass cements have all been used with liquid oxygen. Nonmetallics must be screened for impact sensitivity.

Nitric Acid.

Teflon gaskets are satisfactory.

Nitromethane.

Bakelite is compatible with nitromethane.

Ozone.

Teflon, Kel-F, polyethylene have been used.

Propyl Nitrate.

Teflon, polyethylene, nylon, dacron, orlon, Mylar, bakelite, and Kel-F are satisfactory.

S-E-C-R-E-T

Tetranitromethane.

Tetranitromethane is compatible with organic materials.

UDMH.

Polyethylene, Teflon, Garlock 735, Mylar, Stoner, BS-55 (a butyl rubber), vermiculite, asbestos, glass wool, and magnesium are compatible with UDMH. No lubricant is recommended at present.

The following additional information on Teflon and Kel-F, two very important materials in the liquid propellants picture, may be of additional value:

Teflon.

Teflon is a polymerized fluorine-substituted hydrocarbon, polytetrafluoroethylene. It is chemically resistant to most materials except molten alkali metals and fluorine. It is nonflammable, and its heat resistance continues upward to 500°F. Teflon has excellent machining qualities. It is made from fluorospar and chloroform. Hydrofluoric acid is first made from the fluorospar and is pyrolyzed with chloroform and then by high temperature and pressure polymerization to achieve the final product. Teflon is available from Du Pont, Gering Products, Resistoflex Corporation, and the US Gasket Co.

Kel-F.

Kel-F is another substituted hydrocarbon that has been used in handling liquid propellants. In this case, three fluorine atoms and one chlorine atom are substituted in ethylene, polytrifluorochloroethylene. It is resistant to most everything except halogenated organic solvents. Kel-F is quite resistant to both acid and alkali. It is nonflammable, and its heat resistance continues up to 390°F. Kel-F will break down at a point somewhat below 600°F, and it has excellent machining qualities. It is available from the four companies mentioned above as manufacturing Teflon. In terms of comparable rubber and plastic materials, both Teflon and Kel-F are fairly expensive materials -- especially when large quantities are required.

S-E-C-R-E-T

C. Metallic Materials.

In summarizing the metal requirements, it should be pointed out that the metals have been discussed only from the point of view of their use in the production and storage of the propellants. No mention has been made of the actual metals which might be required inside the engine itself. Metals are discussed here only in terms of the conditions to which they are subjected in processing and in storage. It is obvious that the metal in an engine may be subjected to conditions more extreme than those in the production or storage of the propellant.

The materials that were considered have been fairly common, such as steel, stainless steel, and nickel. Some special materials such as Monel, Inconel, copper, and aluminum have been used largely because of special corrosion problems or low-temperature considerations.

D. Miscellaneous.

This section will attempt to define the problems being faced in applications, particularly with the most common propellants.

Among the monopropellants, hydrogen peroxide is overcoming a production problem. The electrolytic process, used for production up to now, requires a high capital investment and high power cost. It is gradually being replaced by a noncatalytic organic synthesis process which requires lower capital costs, simpler plant operation, and less electrical energy. The propane-oxidation method of Shell is also replacing the high-cost electrolytic process. In the production of hydrazine, still of fair importance among the monopropellants, engineering know-how is the most critical problem.

Among the oxidizers, liquid oxygen faces problems of transportation and storage. With nitric acid the high corrosion rates with many of the materials is the problem. Ozone and fluorine are not sufficiently used or known in their applications to make it possible to say anything more than that ozone is very sensitive and that, of course, fluorine is very toxic and very corrosive. Tetranitromethane has extreme shock sensitivity.

Among the fuels, ethyl alcohol presents no problem except its denaturing requirements. With JP-4 a problem exists in its application

Next 8 Page(s) In Document Exempt

S-E-C-R-E-T

APPENDIX B

ILLUSTRATIONS

- 59 -

S-E-C-R-E-T

S-E-C-R-E-T

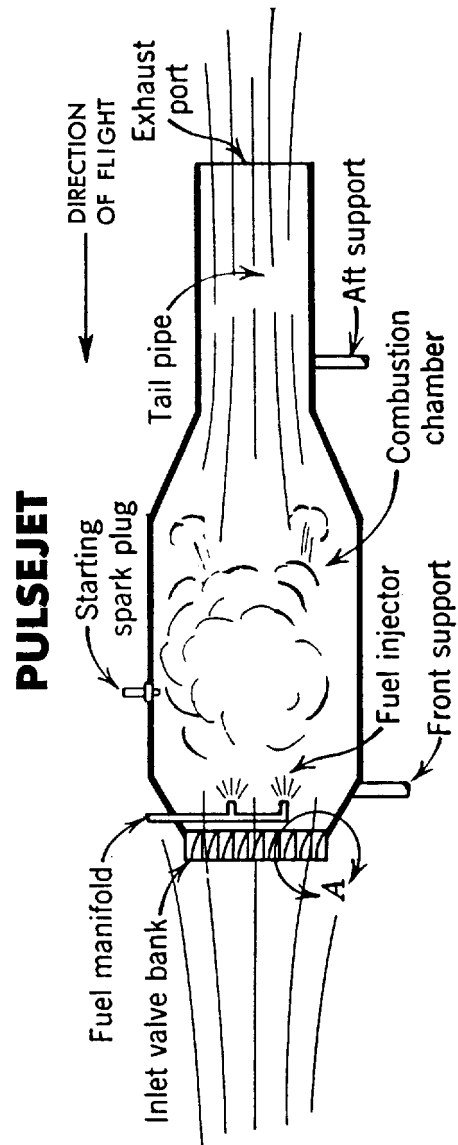


Figure 1

- 61 -

S-E-C-R-E-T

S-E-C-R-E-T

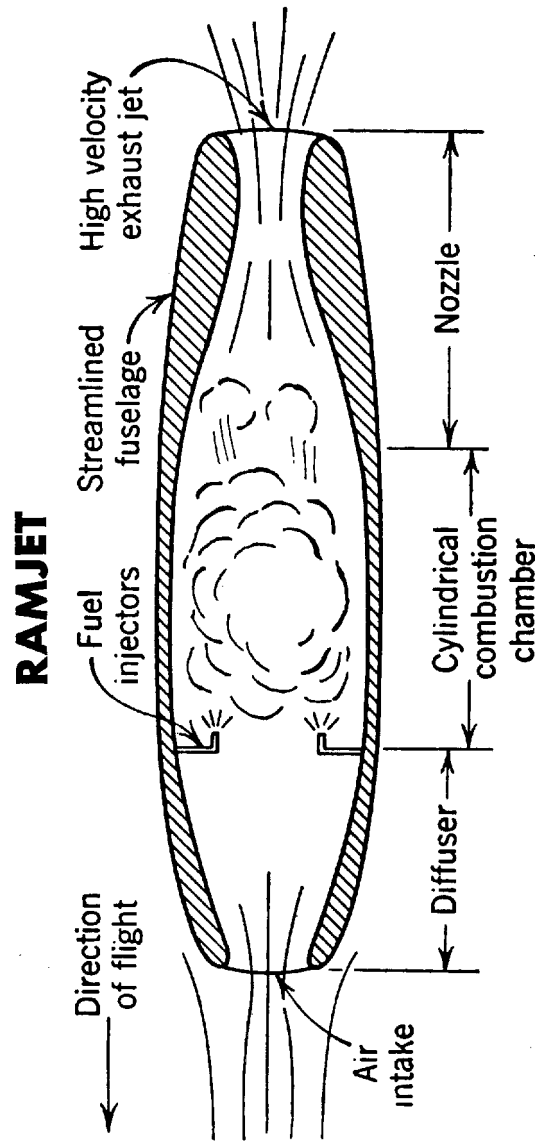


Figure 2

S-E-C-R-E-T

S-E-C-R-E-T

TURBOJET

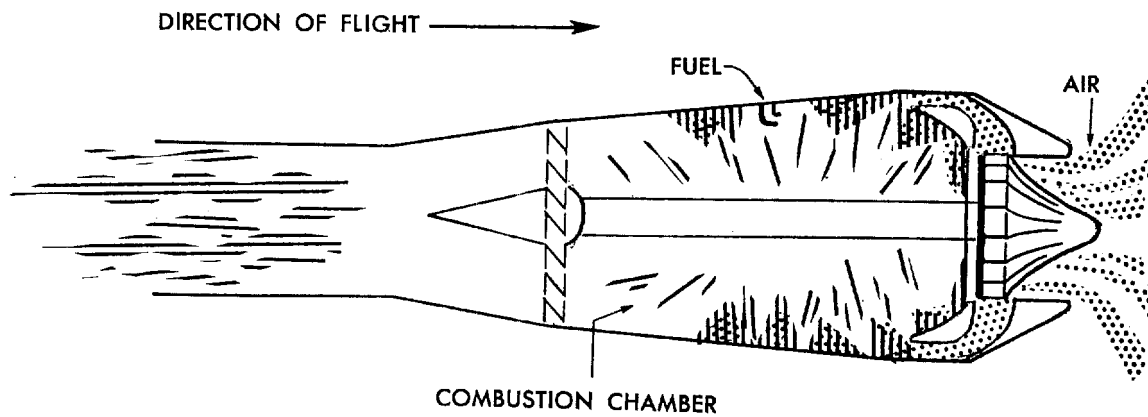


Figure 3

ROCKET

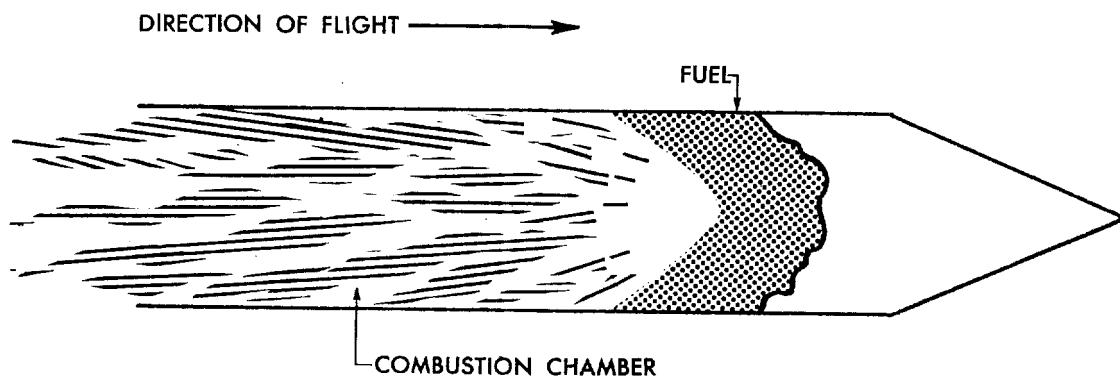


Figure 4

S-E-C-R-E-T

PRINCIPAL ELEMENTS OF BIPROPELLANT UNCOOLED ROCKET MOTOR

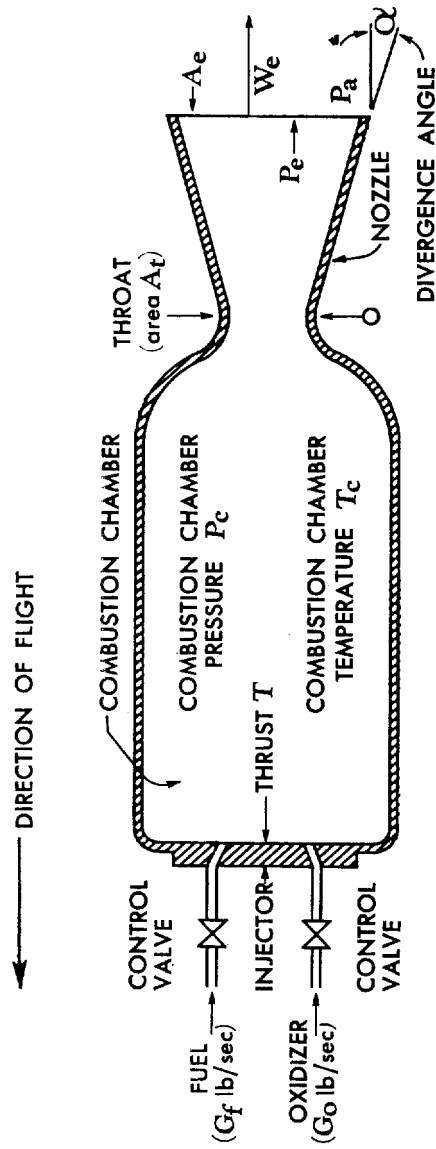


Figure 5

- 67 -

S-E-C-R-E-T

S-E-C-R-E-T

V-2 MOTOR

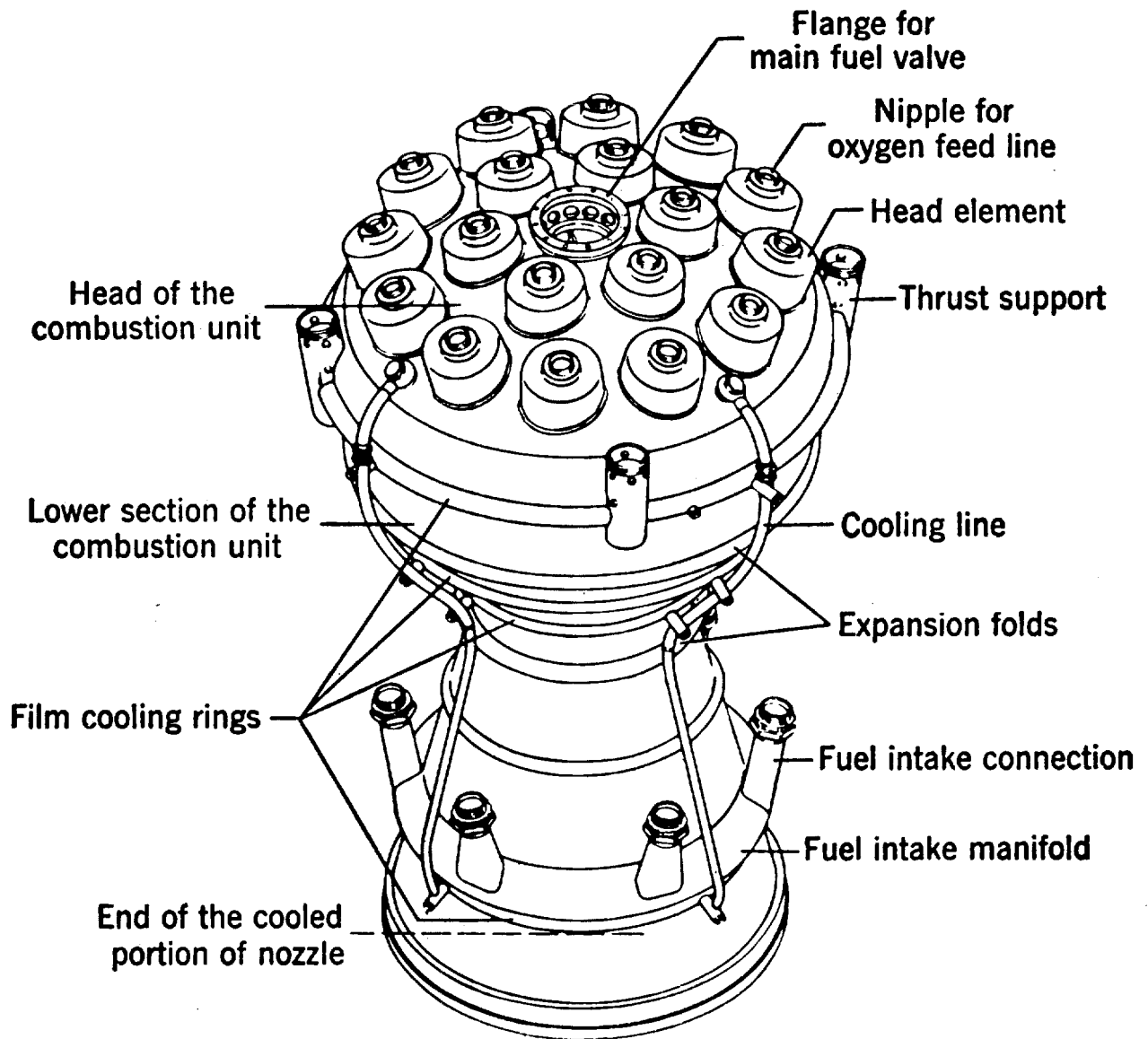


Figure 6

- 69 -

S-E-C-R-E-T

S-E-C-R-E-T

PRESSURIZED BIROPELLANT ROCKET SYSTEM

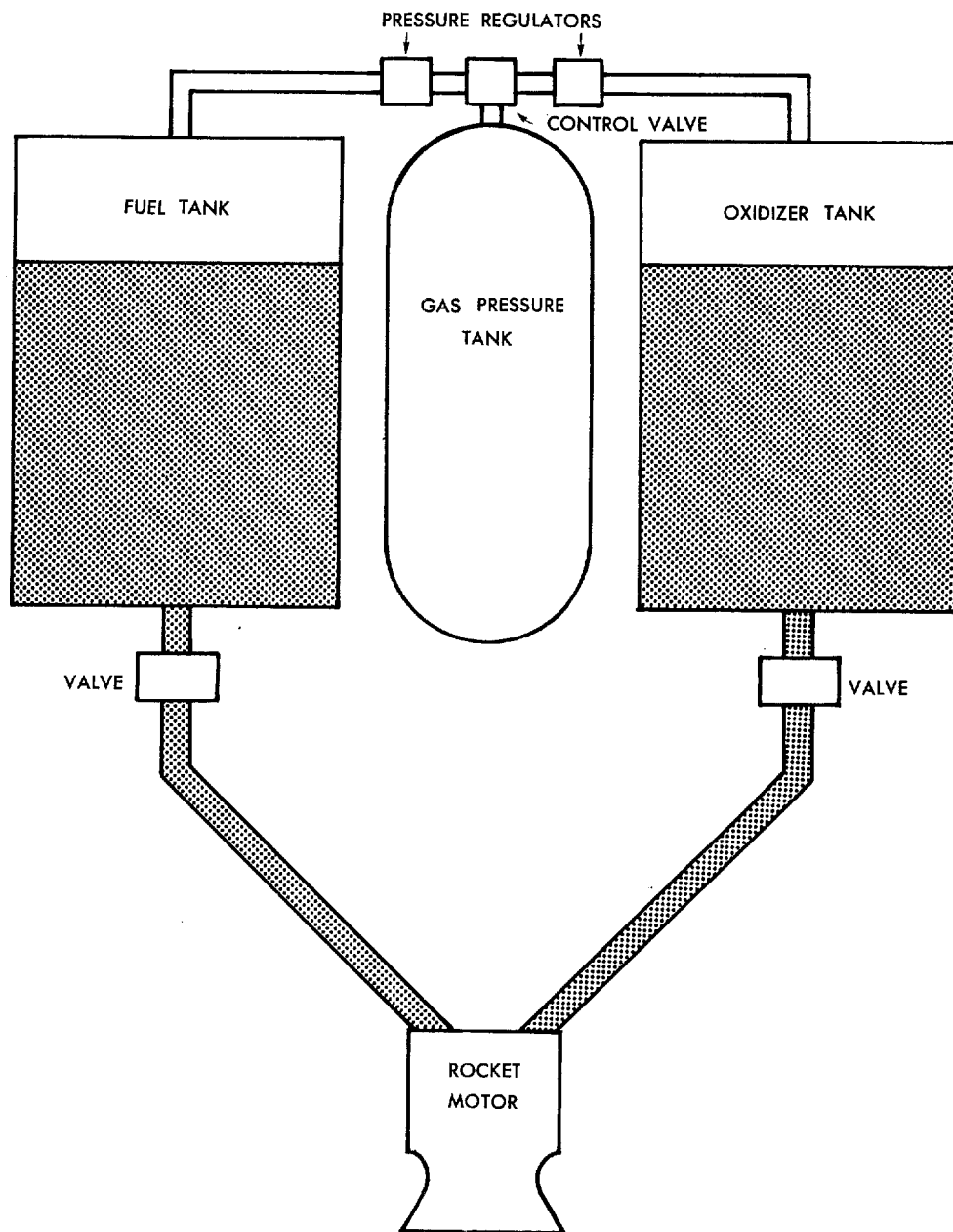


Figure 7

- 71 -

S-E-C-R-E-T

S-E-C-R-E-T

PUMP - TURBINE BIPROPELLANT ROCKET SYSTEM

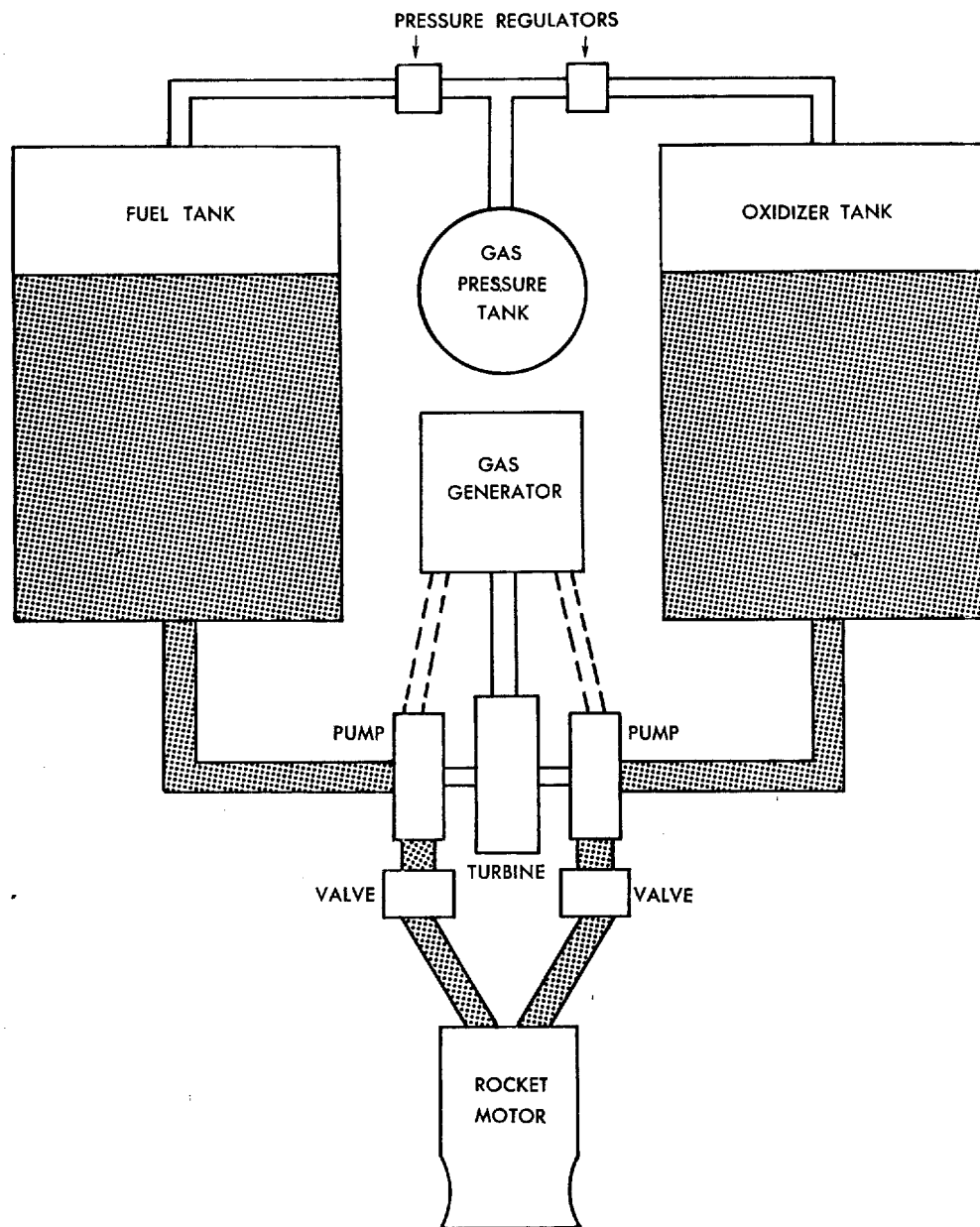


Figure 8

- 73 -

S-E-C-R-E-T

S-E-C-R-E-T

INJECTOR PATTERNS

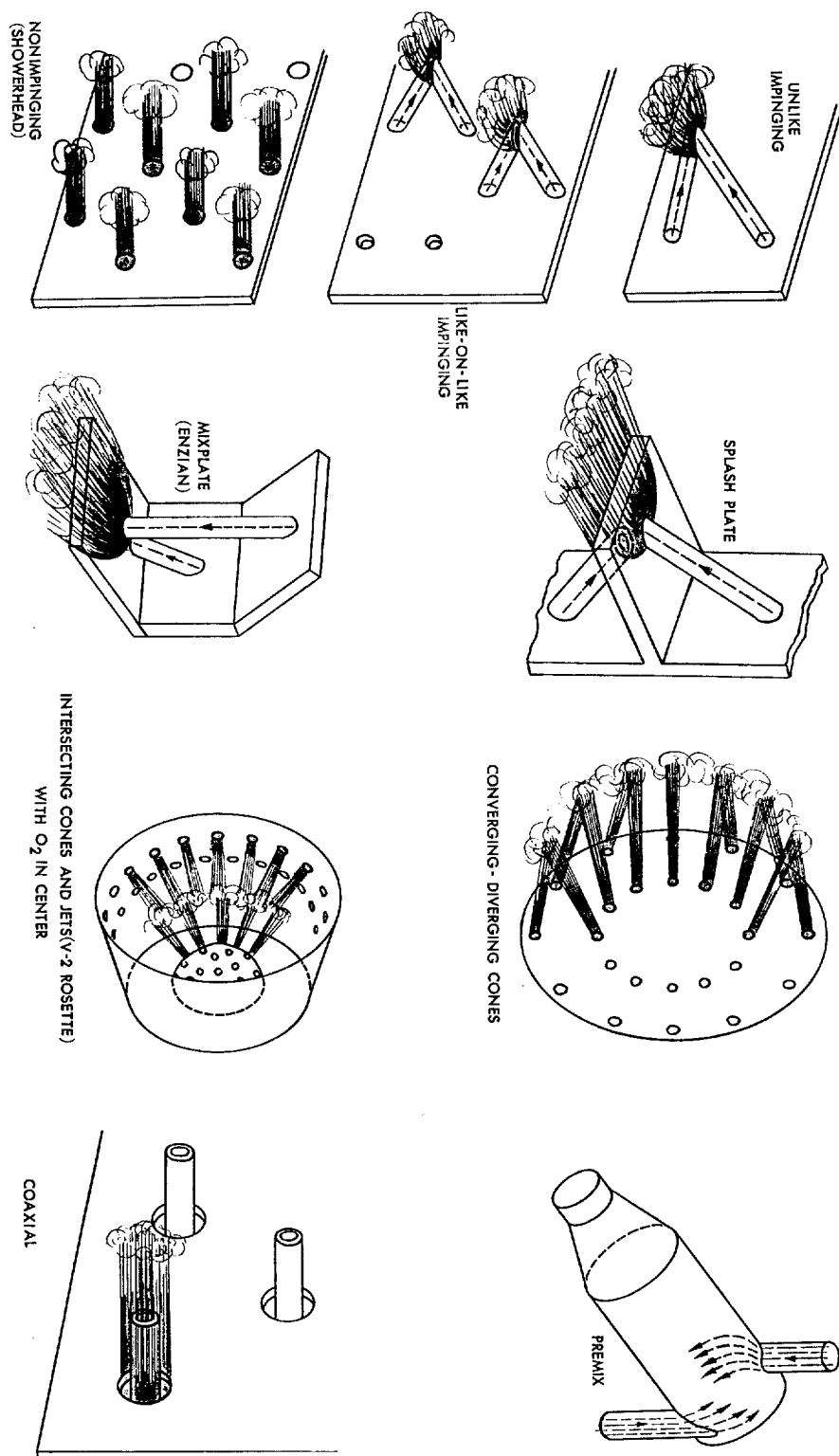


Figure 9

- 75 -

S-E-C-R-E-T

Next 34 Page(s) In Document Exempt